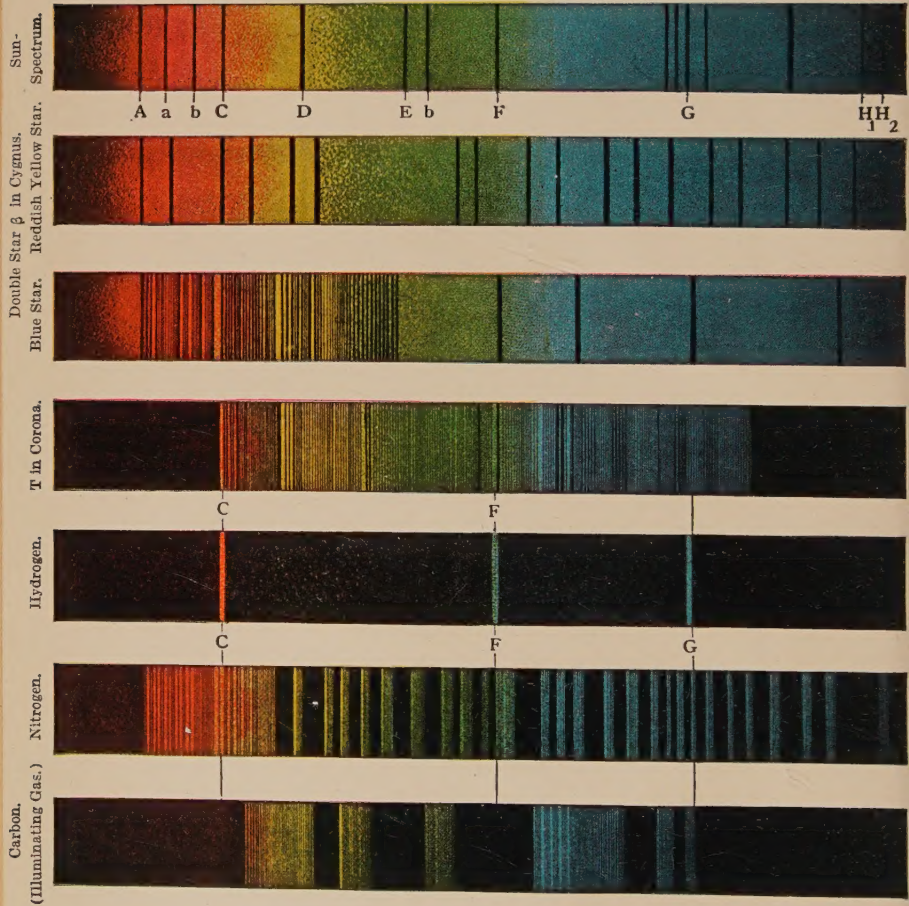




Spectra of the Fixed Stars and Nebulae Compared with the Sun-Spectrum and Other Spectra

HIGH SCHOOL CHEMISTRY

BY

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PREFACE

As a practical study, few subjects in the secondary school course excel chemistry. In the kitchen and laundry, in the garage, in the workshop, around the farm, and in almost every phase of daily life, we find use for chemistry and its applications. As a cultural study, chemistry is also valuable. It makes more intelligible advertising and other matter on radio, automobiles, storage batteries, etc.; it develops the reasoning power and improves the memory; and it enlarges the vocabulary. It demands the precision of mathematics and an exactness of words and endings comparable with a study of foreign languages.

The aim has been to make this book practical and to show the relation of chemistry to everyday life without neglecting the fundamental principles upon which the science is based. Thus the relation of chemistry to water purification, fuels and illuminants, agriculture, paints and varnishes, textiles, paper, etc., is especially emphasized.

The chemical processes have been selected and discussed with a view to illustrate chemical principles. In certain cases the struggles of the men who developed certain processes have been treated briefly to humanize the subject and make it more vital. Throughout the text the author has used simple language, well within the grasp of young pupils of high school age.

Especial effort has been made to develop the chemical theory in a clear, concise, logical manner. Somewhat at variance with the usual custom, the chapters dealing with the atomic theory, atomic and molecular weights, valence and equations have been grouped. The treatment of these chapters is concise, but enough typical cases are studied in

sufficient detail to give the student a clear conception of these fundamental principles as a whole. The author has studied the mistakes of students in their efforts to balance and complete equations, and in the chapter on equations he has attempted to present the subject from the pupils' point of view.

It is the opinion of the author, based upon several years' experience, that the principles of metallurgy can be taught better by means of a few typical metals than by a great variety of them. Thus the reduction of iron ores with carbon as discussed in Chapter XXXI is typical of the processes used in extracting such ores as copper, tin, and zinc. In the later study of such metals the process of extraction is made considerably shorter. In like manner, the electrolysis of bauxite illustrates another important method of extracting metallic elements. The metallurgy of magnesium, calcium, sodium, and potassium is too similar to need much further detailed study.

The chapter on colloids includes such practical applications as the use of foam for fighting fires, froth-flotation for concentrating ores, and Cottrells for precipitating acid mist and smelter dust. Many people believe that the whole science of chemistry had to be revised and rebuilt in the light of War research. Some new compounds were prepared, and several little-used substances were put to military use, but the eternal principles of chemistry were unchanged. A new chapter on chemicals used in war has been included, with a list of applications of such chemicals to peace time uses. Is it too much to hope that some of these new compounds and the new processes of preparing them in quantity, together with the impetus given to research in physiological chemistry, may prove at least a small compensation for the tremendous loss of life and property caused by the World War?

It is probable that many teachers will assign the chapter

on war chemicals to be read rather than studied. For students who will not go to college, certain topics may be omitted to gain time for the study of the chapters on the compounds of carbon. No attempt is made to use smaller type to indicate less important topics, since pupils are apt to assume that matter set in such type is to be omitted. A large number of new illustrations has been added, each being chosen to help clarify a process or principle. Summaries of the chapters have been included, and a list of questions designed to be thought-provoking has been appended.

C. E. D.

Newark, N. J.
Feb., 1925.

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For other illustrations, the author finds it a pleasant duty to express his thanks to the following individuals and manufacturing firms: Acheson Graphite Co.; American Gas Accumulator Co.; American Institute of Mining and Metallurgical Engineers; American Steel and Wire Co.; American Cyanamid Co.; American Water Works and Electric Co.; Anaconda Copper Mining Co.; Berkefeld Filter Co.; Blaugas Company of America; Carborundum Co.; Central Stamping Co.; Chilean Nitrate Propaganda; Colgate & Co.; Combustion Engineering Co.; *Concrete*; Crucible Steel Company of America; Cupra, Inc.; Davenport, E. S.; Demuth Glass Co.; Department of Works, Toronto; Domestic Electric Co.; East Orange Public Library; Foamite Childs Corporation; Ford Motor Co.; General Electric Co.; Goldschmidt Thermit Co.; International Cement Co.; International Oxygen

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HIGH SCHOOL CHEMISTRY



CHAPTER I

MATTER AND ENERGY

1. Chemistry: A Science of the Best-known and Least-known Things. When we place wood, coal, or other fuel on the grate of our stove or furnace and then open the draft for air to enter, we have everything we need for a fire except an increased temperature. By the aid of a match the temperature may be raised until combustion begins. Such burning is one of the most important examples of certain chemical changes that are constantly occurring in nature. It remained for chemistry, one of the youngest of the sciences, to furnish us with an explanation of what really happens when a piece of wood burns, when iron rusts, when milk sours, or when foods decay. See Fig. 1.

The human body is a laboratory in which chemical changes are taking place all the time. Just as we stoke a furnace by adding more coal, so we supply our bodies with fuel in the form of foods. The air which we require for the slow fires within our bodies enters through the lungs, combines with our foods, and the waste products are eliminated by the various organs of excretion.

In the kitchen the cook is making use of practical chemistry. Perhaps she knows nothing of the science, and her "rule of thumb" methods do not always give consistent results. Possibly she was trained in Domestic Science and gets better results because she knows why sour milk and soda make palatable biscuits, while sweet milk and soda produce biscuits that are yellow and bitter.

The garage and the laundry are small laboratories where chemistry may be applied, and that farmer is apt to be most

successful who knows the chemistry of soils and fertilizers. The clothing which we use to protect our bodies is sponged, cleaned, or even fabricated by means of chemistry, while the beautiful colors with which the textiles are dyed are the fruits of long hours of patient research by the color chemist.

The chemist is constantly discovering new and better methods of manufacture. He searches for "contact agents" which by their mere presence speed up chemical processes and



FIG. 1.—An old alchemist's laboratory.

thus save time and money. He finds new uses for the by-products which accumulate during manufacturing operations. He makes our drugs, dyes, medicines, steel, glass, cement, pottery, fertilizers, and hundreds of other products. See Fig. 2.

The boy or girl who wishes to know "how changes occur" and "why things happen" will find chemistry an interesting science. The student who wishes a general education will find in chemistry a subject of broad, cultural value. Those

who become adept in this science may find in it a comfortable living, or the satisfaction of having made some epoch-making discovery.

2. Matter. Everything with which we come into contact is called matter. We detect its presence by the aid of one or more of the senses, as sight, smell, taste, or touch. We may define matter as anything that occupies space or takes up room. In other words, it has volume. All students are



FIG. 2.—A light, well-ventilated, modern laboratory.

familiar with matter in the solid or liquid state, but some persons may question the fact that gases occupy space. When the tornado topples over buildings or blows down trees, we are conscious that the gaseous air is matter. Furthermore, it is impossible to pour water into a bottle unless there is an opening by which the air inside may escape.

3. States of Matter.—There are three states of matter: *solid, liquid, and gaseous*. Solids have a definite volume and a definite shape. They do not need lateral support to maintain their form. In fact most solids are so rigid that they may be

subjected to considerable pressure without becoming distorted. Liquids have a definite volume, but they take the shape of the containing vessel. Gases have neither a definite volume nor a definite shape. They take the shape of the container, and their volume is decidedly changed by a change in temperature or a change in the pressure to which they are subjected. For that reason it is necessary to specify the temperature and pressure when we speak of gas volumes. *The standard temperature at which gases are measured is 0° C.; the standard pressure is one atmosphere, or the pressure which is exerted by a column of mercury 760 mm. high.* For example, if we speak of a quart of oxygen gas, we may specify that it measures one quart when the temperature of the gas is 0° C., and the pressure upon it is equal to 760 mm. of mercury. Both liquids and gases are called *fluids*, from the Latin word *fluere*, meaning to flow.

4. Nature of Matter and the Kinetic Theory. From its behavior, it is quite evident that all matter is made up of very small particles called *molecules*. These particles are so small that they can not be seen even with the most powerful microscope. It would probably take a million molecules laid side by side to make a line one millimeter long. The best estimates show that a liter (approximately one quart) of gas at standard temperature and pressure contains 2.69×10^{22} molecules. It is estimated that if a drop of water were magnified until it became as large as the earth, its molecules, if magnified correspondingly, would be about as big as oranges. Despite so great a number of molecules, the space between the molecules of gases is much greater than that occupied by the molecules themselves. In other words, the molecules of gases are relatively distant neighbors.

Small as the molecules are, they are believed to be made up of *atoms*, much smaller particles that are indivisible by either physical or chemical means. The atom is the chemist's unit from which he builds various compounds. In a later chapter,

when we study radio-activity, we shall learn that certain heavy atoms explode spontaneously, forming lighter atoms and exceedingly small particles called *electrons*.

Several facts show quite conclusively that *the molecules of matter are in rapid motion with respect to one another*. The fact that liquids evaporate is one evidence of such motion. The decided odor of musk, camphor, and naphthalene (moth balls) is proof that the molecules of these solids are in motion. Gas rushes out of a stopcock when it is opened, and gases intermingle even through porous membranes. During the World War, the "mustard" gas evaporated slowly and made its way to every corner of the dugouts. These and other examples furnish proof that the molecules of matter are in motion.

5. Measurement of Matter. Two systems of measurement are in common use, the English system and the Metric system. The English system is probably well enough known so that it need not be discussed here.

The Metric system is a decimal system. The unit of length is the *meter*. It is divided into tenths, or *deci*-meters; into hundredths, or *centi*-meters; and into thousandths, or *milli*-meters. Ten meters make 1 *deka*-meter; 100 meters, 1 *hekto*-meter; and 1000 meters, 1 *kilo*-meter. Arranged in tabular form:

10 millimeters (mm.)	make 1 centimeter (cm.).
10 centimeters (cm.)	make 1 decimeter (dm.).
10 decimeters (dm.)	make 1 meter (m.).
10 meters (m.)	make 1 dekameter (Dm.).
10 dekameters (Dm.)	make 1 hektometer (Hm.).
10 hektometers (Hm.)	make 1 kilometer (Km.).

The meter equals 39.37 inches; 1 inch equals 2.54 centimeters. See Fig. 3.

The metric unit of capacity is the *liter*. The same prefixes are used as in the table of lengths. A cubical box 10

centimeters on a side holds 1 liter; thus it is equivalent to 1000 cubic centimeters, or 1 cubic decimeter. It is slightly

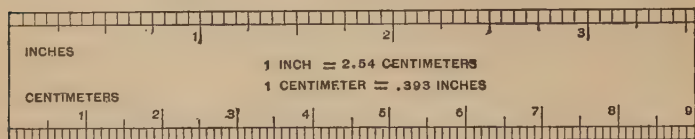


FIG. 3.—Comparison of Metric and English units of length.

smaller than the *dry* quart and a little larger than the *liquid* quart. See Fig. 4.

The metric unit of weight is the *gram*. The same prefixes are used as in the table of lengths. *One liter of distilled water at 4° C., weighs 1 kilogram.* Therefore 1 cubic centimeter of water weighs 1 gram. The student will do well to remember that a nickel weighs almost exactly 5 grams. The kilogram weight equals a little more than 2.2 lb.; 1 oz. is a little

more than 28 gm. See Fig. 5. The student should memorize the ratios 2.54, 39.37, and 2.2.

6. Energy. *Energy is the capacity for doing work.* It requires some form of energy to produce motion in matter.

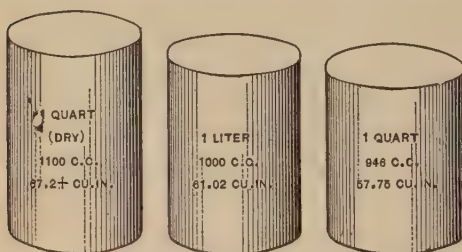


FIG. 4.—Comparison of Metric and English units of capacity.

In fact to bring about any change in the condition of matter energy is needed. In turn, changes in matter itself may liberate various forms of energy.

7. Kinds of Energy. There are several kinds of energy: *mechanical energy; heat energy; electrical energy; light energy; and chemical energy.* For doing chemical work all of the above-named are used extensively. *Energy can not be de-*

stroyed. It is possible to *convert* or *transform* one kind of energy into a different form. Thus it is possible to use heat energy from burning coal to produce steam; the steam may be used in a steam engine to furnish mechanical energy; electrical energy may be generated by a dynamo turned by such mechanical energy; and electrical energy may in turn be easily transformed into heat, light, or mechanical energy. The fact that energy can not be destroyed is known as the *Law of the Conservation of Energy*.

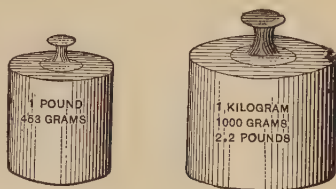


FIG. 5.—Comparison of Metric and English units of weight.

SUMMARY

Chemistry is a cultural study because it answers many important questions. It is intensely practical, because it is an important factor in manufacturing and industrial operations.

Matter is anything that occupies space.

There are three states of matter: *solid*, *liquid*, and *gaseous*.

According to the kinetic theory, *matter is made up of molecules; these molecules are in very rapid motion*.

The Metric system is used extensively in scientific work. The *meter* is the unit of length; the *liter*, the unit of capacity; and the *gram*, the unit of weight. In the laboratory solids are usually measured by weight; gases by volume; and liquids by either volume or weight.

Energy is the capacity for doing work. There are several kinds of energy: *mechanical*, *heat*, *light*, *electrical*, and *chemical* energy.

PROBLEMS

1. Find the number of grams in a pound. Find your weight in kilograms.

2. Reduce your height to meters. Find the value of 10 Km. in miles.

3. What must be the dimensions in decimeters of a cubical box

whose capacity is 1 liter? How many cubic centimeters are there in 22.4 liters?

~~4.~~ A pneumatic trough is 30 cm. long, 2 dm. wide, and 80 mm. deep. What is its capacity in c. c.? In liters?

~~5.~~ A bottle holds 1650 c. c. How many grams of water does it hold? How many liters? {How many kilograms? }

~~6.~~ A test tube 6 in. long has an internal diameter of $\frac{3}{4}$ in. How many c. c. does it hold?

~~7.~~ Measure the length of this page in inches. Reduce this measurement to centimeters.

CHAPTER II

ELEMENTS—MIXTURES—COMPOUNDS

8. Introductory. In our study of chemistry, we shall often have occasion to use the terms: *element*, *mixture*, and *compound*. The number of elements known is not very great, but thousands of mixtures and compounds are known, and the number is constantly increasing. Since chemistry is the science that deals with elements and compounds and the chemical changes which they undergo, the beginner must acquire a definite concept of each of these three terms.

9. The Element is the Limit of Analysis. We may start with a complex substance, or a chemical compound, and separate it into simpler substances by analysis. We soon reach a point, however, where the constituents do not yield to further subdivision. For example, if we pass an electric current through water containing a little acid, the water is readily decomposed into two elements, hydrogen and oxygen. We call the hydrogen and oxygen *elements because all attempts to split them up into simpler substances have resulted in failure*. Within the last thirty years chemists have learned that some so-called elements do explode spontaneously, but in all *analytical* work the *element* is considered the chemist's unit.

It is quite impossible to prove that any given substance is an element. We know that no one has yet succeeded in decomposing oxygen into anything simpler, but we can not prove that some one may not succeed in doing so in the future by the use of some as yet untried method. The old Greeks considered fire, earth, air, and water as elements. In fact water was considered an element until Cavendish in

1766 recognized hydrogen as an element and found that it would unite with oxygen to form water. Later it was named hydrogen (water producer) by Lavoisier.

10. Number and Distribution of the Elements. At the present time about eighty-five substances are known that chemists have good reason to believe are elements. New elements are being discovered from time to time. Such substances as copper, oxygen, lead, silver, gold, and iron have been tested in almost every conceivable manner without their decomposition into other substances. Of the eighty-odd elements known, only about thirty are well known. The names of many elements are not familiar, even to well-educated persons. The student will be interested in comparing the list of fairly common elements given on page 14 with the more complete list given on the inside of the back cover.

According to an estimate made by Clarke, about 98% of the earth's crust (near the surface only) is composed of eight elements in about the following proportion:

Oxygen.....	47.0%	Calcium.....	3.4%
Silicon.....	28.0	Magnesium.....	2.4
Aluminum.....	7.9	Sodium.....	2.4
Iron.....	4.4	Potassium.....	2.4

11. Metals and Non-metals. Elements are divided into two classes: *metals* and *non-metals*. The *metals* have a luster like steel or silver. They are good conductors of heat and electricity. Chemically they are *alkali-* and *base-formers*. Copper, zinc, tin, iron, lead, and silver are all *metals*. Sulfur and phosphorus are good examples of *non-metals*. They often have a waxy or glassy luster, and they are poor conductors of heat or electricity. Chemically they are *acid-formers*. The gaseous elements, hydrogen, nitrogen, oxygen, chlorine, etc., are also examples of non-metals. The division line is not sharply defined, since such elements as arsenic and antimony

have some metallic and some non-metallic properties. Such elements are sometimes called *metalloids*.

12. Names of Elements. Metals recently discovered have the Latinized ending "um" or "ium." Sodium, calcium, potassium, radium, and aluminum are examples. The root or stem used may be taken from some characteristic property of the element, from the source from which it is obtained, or it may be the name of the country in which it was discovered. For example, radium is a radio-active element; aluminum was obtained from alum; and scandium was discovered in Scandinavia. Helium is a non-metal that has the ending "ium," but it was discovered in the sun's atmosphere before it was found on the earth, and it was believed to be metallic. Non-metals generally take the ending "on," "in," or "en." Carbon, chlorin, and oxygen are examples. The elements known to the ancients, copper, lead, tin, iron, mercury, etc., do not take the regular endings.

13. Symbols of Elements. For convenience, symbols are used to designate elements. They serve as abbreviations, but the student will learn that a symbol means more than an abbreviation. For example, the letter O is used to represent oxygen; it also means one atom of oxygen, or the smallest particle of oxygen that can enter into combination with other elements. Usually the first letter of the name of an element is used as its symbol, as H for hydrogen, N for nitrogen, or C for carbon. When the names of several elements begin with the same letter, some other letter is used with the initial letter, as Cl for chlorin, Ca for calcium, and Cr for chromium. In several cases the symbol is derived from the Latin name for the element. Thus Fe from the Latin word *ferrum* is the symbol for iron; Pb from the Latin word *plumbum* is the symbol for lead; and Na from *natrium* is the symbol for sodium. The following table gives the names and symbols of some of the common elements;

ELEMENTS—MIXTURES—COMPOUNDS

Aluminum...Al	Iodin.....I	Platinum...Pt
Arsenic.....As	Iron.....Fe	Potassium...K
Bromin.....Br	Lead.....Pb	Radium....Ra
Calcium....Ca	Magnesium Mg	Silicon....Si
Carbon.....C	Manganese Mn	Silver.....Ag
Chlorin....Cl	Mercury...Hg	Sodium....Na
Chromium...Cr	Nickel....Ni	Sulfur.....S
Copper.....Cu	Nitrogen...N	Tin.....Sn
Gold.....Au	Oxygen....O	Tungsten...W
Hydrogen...H	Phosphorus P	Zinc.....Zn

14. Mixtures and Compounds. When matter is made up of two or more elements, they may be mechanically mixed, or they may be chemically combined. The following experiment serves to show the differences between a *mixture* and a *compound*. If we put some iron filings on a piece of paper and add to them a little powdered sulfur, there is no apparent action between them. No heat is gained or lost, no light is emitted, and there is no evidence that electricity is produced. In other words, there is no evidence that chemical action is taking place. The two elements may be *mixed* in any proportion, equal parts, two to one, or one to one hundred. If we pass a magnet over the mixture, the iron filings will cling to the magnet and may thus be separated from the sulfur.

Next let us put the mixture into a test tube and heat it rather gently. The contents of the tube begin to glow, and even if the external heat is withdrawn, the whole mass soon becomes red hot. Subsequent examination of the product in the tube shows that an entirely new substance has been formed. It does not resemble either the iron or the sulfur. The product is a *compound*. The iron can not be removed by means of a magnet. The sulfur can not be picked out mechanically. If we decompose the compound by chemical means and analyze it carefully, we find that it was composed of 7 parts by weight of iron and 4 parts by weight of sulfur. If we had started with a different ratio, any excess of either element would have been left uncombined. The several

differences between a mixture and a compound are summarized in the following contrasting table:

MIXTURE

In a mixture the constituents may be present in any proportion.

In preparing a mixture, there is no evidence of any chemical action, such as the evolution of heat, light, gas, or electricity.

A mixture may often be separated by mechanical means.

COMPOUND

A compound always has a definite composition by weight.

In the preparation of a compound, some evidence of chemical action is apparent. Heat or light may be emitted or absorbed, an electric current produced, or a gas liberated.

The constituents of a compound can be isolated by chemical means only.

Air, baking powder, hash, granite, and the various kinds of soils are examples of mixtures. Water, salt, sugar, marble, alcohol, and sulfuric acid are examples of compounds.

15. Law of Definite Proportions. An English school-master, John Dalton, was the first to call attention to the chief difference between mixtures and compounds. He observed that the constituents of a compound are always present in the same proportion by weight. This characteristic of a compound is clearly formulated in Dalton's law of definite composition or proportion: *Every compound has a definite composition by weight.* The law is so exact that a manufacturer of chemicals knows exactly how much of each element to use in making compounds. It is the fundamental law upon which the whole science of chemistry is based. Without it, chemistry would be a jumble of unrelated facts.

16. Formulas of Compounds. A formula is often used by the chemist to show of what elements a compound is made up. The formula for water is H_2O . This formula represents 1 molecule of water. It shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen.

If we write $2\text{H}_2\text{O}$, the expression represents 2 molecules of water, each containing 2 hydrogen atoms and 1 oxygen atom. The number before a formula always shows the number of molecules taken; the number following each symbol shows the number of atoms of that element in each molecule of that compound. The formula for sulfuric acid is H_2SO_4 . It means that each molecule of sulfuric acid is made up of two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen.

17. Properties of Elements and Compounds. We identify elements and compounds by means of their properties. There are certain *general* properties common to all matter. Of course such properties are of no value for identification purposes. However, all substances have certain *special* properties by means of which we recognize them. The more peculiar the properties of a substance, the easier it is to identify it. Alcohol is easily recognized by its peculiar odor. Ammonia may be detected by its odor. Table salt may be identified by its taste. Since the number of compounds that may be formed from the elements is almost infinite, the only method suitable for the chemist is to classify compounds according to *similar* properties, and then identify each one by its *peculiar* individual properties.

The use to which a substance is put depends upon its properties. We use copper for electrical wires because it is the best conductor known except silver. We use aluminum for cooking utensils since it is clean, light, and a good conductor of heat. Hydrogen is used for filling balloons as it is the lightest gas known. While the student may sometimes find the study of properties a little irksome, yet such study is essential if one is interested in identifying substances or determining the uses for which they are fitted.

In studying properties we must distinguish between *physical* and *chemical* properties. Under physical properties are included *color, odor, taste, solubility in water, hardness,*

density, conductivity of heat and electricity, tenacity, ductility, and malleability. Under chemical properties we include all chemical activity such as the interaction of the substance with *water, air, acids, and alkalis.*

SUMMARY

Matter is made up of elements, mixtures, and compounds. Elements and compounds are called *substances*. An element is the chemical unit of analysis. About eighty-five elements are known. About thirty elements are common, and only about eight may be classed as occurring abundantly. Elements are classified as *metals* and *non-metals*.

A material made up of two or more elements is either a *mixture* or a *compound*. If the elements are chemically combined and their proportion is definite, the substance is a compound. In a mixture the elements may be in any proportion.

Symbols are used to represent elements. A group of symbols used to show the composition of a compound is known as a *chemical formula*.

QUESTIONS

1. Name five elements; four compounds; three mixtures.
2. If you were given a mixture of sand and sugar, how could you separate them?
3. How could you separate the iron from a mixture of iron filings and sulfur?
4. State some of the characteristic properties of (a) gasoline, (b) alcohol, (c) gold, (d) copper, (e) silver.
5. How would you distinguish between alcohol and gasoline? How would you tell gold from copper? Salt from sugar?
6. Why has the concept of the element changed from time to time?
7. What is the significance of the formula, HNO_3 ? Of KClO_3 ? Of HgO ?

CHAPTER III

CHANGES IN MATTER

18. Physical and Chemical Changes. Ice melts, water changes to steam, liquids freeze, glass breaks, and sugar dissolves in water. We may magnetize a piece of iron or we may pass an electric current through a copper wire. In all cases the matter undergoes some change. Its form may be different or it may change its state, but in no case has the substance lost its identity. Its *molecule* has not been broken up. *The change is physical. Physics is defined as the science that deals with physical changes in matter.*

Wood burns, iron rusts, milk sours, plants decay, and acids interact with metals. In all these cases matter is being changed. The identity of each substance is lost, and a new substance with new properties is formed. *The change is chemical.* In some cases the original molecule is torn down into simpler molecules. In other cases two elements have united to form a new molecule. It quite often happens, too, that the atoms rearrange themselves in the molecule, thus changing the properties decidedly. *Chemistry is defined as the science that deals with chemical changes; it also includes a study of elements and compounds.*

19. How Chemical Changes Are Started. Wood does not begin to burn until it is strongly heated. Rubbing the head of a match over a rough surface causes it to be ignited by the heat of friction. Heat also causes a chemical change in the baking of bread and the cooking of foods. An increase in temperature of 10° C. nearly doubles the speed at which a chemical reaction occurs. Foods cook in about one-fourth the time in a cooker under 20 lb. added pressure that they do

at ordinary atmospheric pressure, because the temperature is increased more than 20° Centigrade. Therefore we conclude that *heat* aids chemical action.

Every one knows that certain colors fade in sunlight. The student knows that a photographic plate is affected when exposed to the *light*. Plants need sunlight for making starch out of the raw materials obtained from the air and soil. A plant kept in the dark soon loses its green color and becomes unable to manufacture its food. These are all examples of the action of light in producing chemical change. The fact that many chemicals, such as hydrogen peroxid, are kept in dark-colored bottles is further indication that light is a very active agent in producing chemical changes.

When an electric current is passed through water to which a few drops of sulfuric acid have been added, decomposition occurs and the elements hydrogen and oxygen are liberated. Many compounds, when melted, or dissolved in water, may be separated into their elements by the passage of an *electric current* through the molten mass, or the water solution. Electricity is used commercially in the refining of metals, in electroplating, and in electrotyping.

Many substances that show no chemical action when they are mixed in the *dry* state, interact readily when in *solution*. Baking powder is a mixture of compounds that remains unchanged if kept dry; as soon as water is added, a chemical change occurs. Light causes a chemical change in making blueprints. The blueprints are developed by the addition of water, which causes a second chemical change.

In conclusion, we find that *heat*, *light*, *electricity*, and *solution in water* are all active in aiding chemical change or in its acceleration.

20. Energy Involved in Chemical Changes. We have just learned that heat may start a chemical change. It is also interesting to note that heat energy is often evolved as such chemical action proceeds. For example, external heat

is used to start a fire, but heat is liberated continuously after the fire is once started until all the fuel is burned.

A chemical reaction that liberates heat as it progresses is said to be *exothermic*.

A reaction that absorbs heat during its progress is said to be *endothermic*. Unless external heat be applied constantly, the action stops.

Other forms of energy are often attendant upon chemical change. Light energy may be evolved, or it may be used to produce the change. Electricity is often produced as a chemical reaction occurs. In a voltaic cell the negative plate is acted upon chemically and the chemical energy is transformed into electrical energy. Even mechanical energy may be liberated during chemical action, as in the detonation of such substances as nitroglycerin and dynamite, or in the explosion of gunpowder.

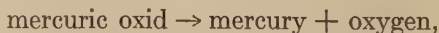
21. Types of Chemical Change. (1) *Analysis*. When an electric current is passed through water as described in section 19, the water is broken up into its elements, hydrogen and oxygen.

The word equation,



is read as follows: water forms (when decomposed) hydrogen and oxygen. In all chemical equations the arrow is read "forms," "gives," or "produces." The plus sign is read "and."

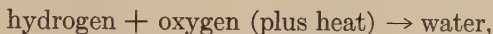
Heating mercuric oxid decomposes it into mercury and oxygen. The equation,



is read as follows: mercuric oxid (heated) "produces" mercury and oxygen. Both these examples are typical of a large number of chemical changes in which a compound is decom-

posed into its elements. *The separation of a compound into its elements is called analysis, or decomposition.*

(2) *Synthesis.* By mixing oxygen and hydrogen and heating the mixture, an explosion occurs. The product formed is water. The equation,



is just the reverse of the one shown under analysis. Here the elements unite to form a compound. *The building up of a compound by the direct union of its elements is called synthesis, or composition.* It quite often happens in chemistry that a different agent or different treatment may cause a complete reversal in the direction of a chemical reaction. To show that a reaction is *reversible*, two arrows, pointing in opposite directions are often used. For example, the double arrow in the equation,



shows that under certain conditions water may be formed by the union of its elements, and that under other conditions water decomposes, yielding hydrogen and oxygen.

(3) *Substitution.* Suppose we suspend a strip of zinc in a solution of some compound of lead. The zinc goes into solution and metallic lead is formed as shown in Fig. 6. The equation,



shows that the zinc has substituted itself for the lead. *A chemical reaction in which one element takes the place of another, or is substituted for another, is known as substitution.* In Fig. 7, we see that zinc will also displace tin from its compounds by substitution.

(4) *Metathesis.* Very often in the laboratory the chemist

mixes solutions of two compounds. In such cases a *double substitution* may occur. When we mix solutions of silver

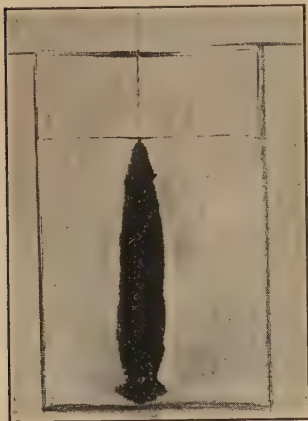


FIG. 6.—The zinc strip goes into solution, displacing the lead which is deposited in the form of crystals.

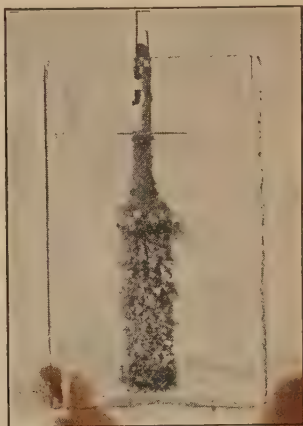
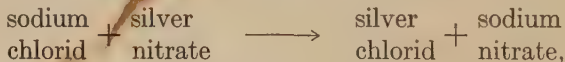


FIG. 7.—The zinc goes into solution, displacing the tin. (Substitution.)

nitrate and sodium chlorid, for example, the sodium and the silver exchange places. The equation,



shows that the sodium and silver have changed partners. *Such double substitution, or change of partners, is called metathesis.* It is sometimes known as *double decomposition*.

The great majority of chemical changes are included under the following classes: *analysis, synthesis, substitution, or metathesis.*

SUMMARY

Changes in matter are *physical* or *chemical*; in a physical change the characteristic properties of the substance are not lost; in a chemical change a new substance with new properties is formed.

Heat, light, electricity, and solution aid chemical changes.

When heat is liberated during a chemical change, the reaction is said to be *exothermic*; when heat is absorbed during the change, we have an example of an *endothermic* reaction.

Physics deals with physical changes; chemistry deals with chemical changes and the study of elements and compounds.

The union of two elements to form a compound is known as *synthesis*. *Analysis* is the decomposition of a compound into its elements. *Substitution* is a chemical change in which one element takes the place of another. In *metathesis*, two compounds decompose, and their elements interchange to form new compounds.

QUESTIONS

1. State whether the following changes are chemical or physical:

- | | |
|---------------------------------|--------------------------------|
| (a) The burning of wood. | (b) The souring of milk. |
| (c) The fermentation of sugar. | (d) Weaving cotton cloth. |
| (e) The decay of food. | (f) Melting of lard. |
| (g) Tarnishing of brass. | (h) Rusting of iron. |
| (i) The evaporation of alcohol. | (j) The explosion of dynamite. |

2. Formerly it was customary to mix soda and sour milk directly when used for baking; now it is customary to mix the soda with the flour and then add the sour milk. Is there a good reason for the latter practice?

3. Which of the chemical changes of question 1 are exothermic?

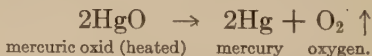
CHAPTER IV

OXYGEN

22. Occurrence. No element is more important than oxygen and no other is so widely distributed. The air we breathe is more than 20% oxygen, and the water we drink is more than 88% oxygen. The clay, sand, and limestone of which the earth's crust is so largely made up, contain about 50% of this element. Oxygen is also present in all plant and animal tissues.

23. Preparation. As a rule there are several ways of preparing elements or compounds in chemistry. In the laboratory we select the one that is most convenient or best illustrates some principle. In commercial work, the cost of the raw material and the value of the by-products obtained have an important bearing on the method selected. Four methods of preparing oxygen are given here:

1. *Heating mercuric oxid.* (Historical.) In 1774 Joseph Priestley focussed the sun's rays upon a red powder, known to chemists as *mercuric oxid*. This compound contains mercury and oxygen. When this red powder is strongly heated it decomposes, yielding mercury and oxygen.



An upward pointing arrow indicates that the product is gaseous; a downward pointing arrow indicates that a solid is precipitated.

This is an expensive method of preparing oxygen and is of historic interest only. Priestley did not call the active gas which he thus discovered oxygen. He described it as a gas

having about the same properties as air, but in "greater perfection." It was named *oxygen* (acid producer) by Lavoisier.

Scheele, a Swedish chemist, working independently discovered oxygen at about the same time, but his results were not published until 1777.

2. *Heating a Mixture of Manganese Dioxid and Potassium Chlorate.* (Usual laboratory method.) Potassium chlorate

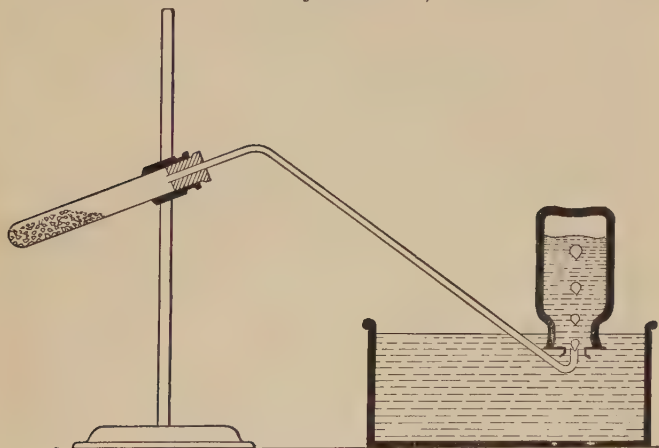
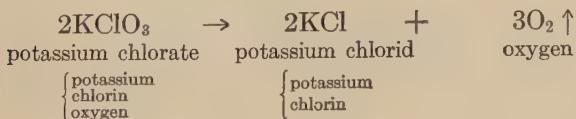


FIG. 8.—Apparatus for preparing oxygen.

is a white, crystalline solid consisting of potassium, chlorin, and oxygen. About 39% of its weight is oxygen. When this compound is heated, either alone or mixed with manganese dioxid, decomposition occurs and oxygen is set free. The gas is not very soluble, hence it may be collected by water displacement. See Fig. 8. The following equation shows how decomposition occurs:



The oxygen comes from the potassium chlorate, and the manganese dioxid serves only as a *catalytic agent*. When it is present the decomposition of the potassium chlorate proceeds more rapidly, the evolution of the gas is more regular, and the temperature needed is much lower. The manganese dioxid appears to be unchanged at the end of the reaction. *Any substance which by its presence aids in producing or accelerating chemical action without itself being permanently changed is called a catalytic or contact agent.* It is similar to the action of a whip on a horse; without helping the horse it makes him go faster. Many chemical reactions proceed so slowly that the success of many manufacturing processes depends upon the use of suitable contact agents. On the other hand, it is often desirable to retard certain reactions.

Some *negative catalysts* are known. For example, acetanilid is added to hydrogen peroxid to retard its decomposition.

3. *Electrolysis of Water.* (Commercial.) We have already learned that water may be decomposed by passing an electric current through water that contains a little sulfuric acid. The acid makes the water a conductor. *Electrolysis is the decomposition of a compound by means of an electric current.* In this case, the oxygen is liber-

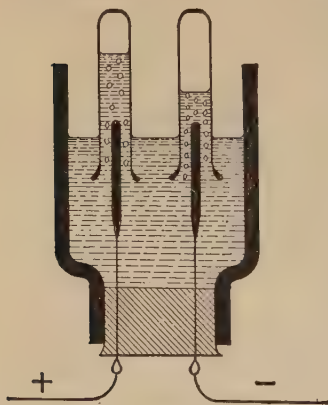


FIG. 9.—Apparatus for the electrolysis of water.

ated at the positive terminal and hydrogen at the negative terminal. See Fig. 9. This method is used on a large scale for preparing oxygen, although sodium hydroxid (concentrated lye) is used instead of the acid. The oxygen is forced into steel cylinders under high pressure. This is the general method of preparing gases for the market. See Fig. 10.

4. *From Liquid Air.* (Commercial.) Oxygen is also prepared commercially by separating it from the other elements in the air. Such separation is possible, because nitrogen and

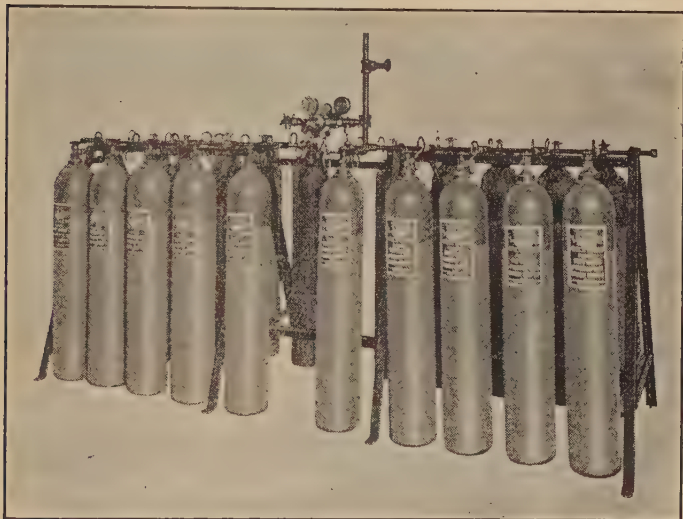


FIG. 10.—Steel cylinders for storing oxygen gas under pressure.

oxygen have different boiling points. When air is liquefied, the nitrogen boils off first, leaving nearly pure oxygen.

24. Physical Properties. Pure oxygen is a colorless, odorless, tasteless gas. It is slightly heavier than air. At standard conditions of temperature and pressure (0°C . and a pressure of 760 mm. of mercury), 1 liter of oxygen weighs almost 1.43 gm. One liter of air under the same conditions weighs a trifle more than 1.29 gm. Oxygen is slightly soluble in water. One hundred liters of ice water will dissolve nearly five liters of oxygen (S. T. P.). It is interesting to note that 100 liters of water at room temperature can hold only a trifle more than 3 liters of oxygen. Therefore if water saturated with oxygen gas at 0°C . were warmed to room

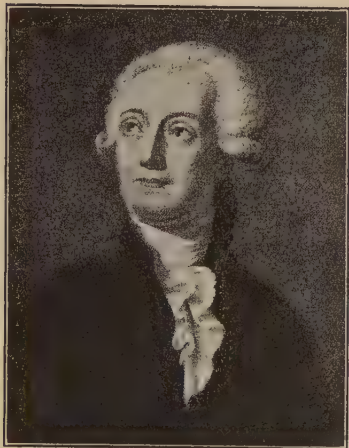
temperature (20° C.), about two liters of oxygen would be expelled. This explains why bubbles of gas appear when a glass of cold water is permitted to stand for some time in a warm room. Only a part of the gas bubbles is oxygen, but all gases are less soluble in warm water than in cold. Like all gases, if cooled sufficiently while the pressure upon it is increased, oxygen is converted into a liquid. Liquid oxygen is pale blue in color.

25. Chemical Properties. Oxygen has been described as an affectionate element. It combines readily with so many other elements. Its most important chemical property is its *activity*. At ordinary temperatures, however, oxygen interacts *slowly* with substances or in some cases not at all. At higher temperatures it reacts *rapidly* with most substances, usually with the evolution of both heat and light.

26. Oxidation. *The process by which oxygen unites with some other substance is called oxidation.* It may occur slowly, in which case it is not generally accompanied by light or noticeable heat, or it may occur rapidly. The union of the oxygen we breathe with the food we eat is an example of *slow oxidation*. Heat is evolved in this case just fast enough to keep the temperature of the body a little more than 98° F. The decay of wood and vegetable matter, and the rusting of certain metals, are other examples of slow oxidation.

The oxygen may be furnished by the air or by some substance rich in oxygen. If a compound *gives up* its oxygen to a substance more readily than the air does, we call it a *good oxidizing agent*. Potassium chlorate is an example.

The compound formed by the union of oxygen with some other element is called an *oxid*. The oxidation of hydrogen forms hydrogen oxid, or water. Carbon plus oxygen forms carbon dioxid. In chemistry a *binary* compound (containing two elements) has the ending "id." A chlorid contains chlorin and some other element.



Antoine Laurent Lavoisier (1743–1794), a French investigator, is called the founder of modern chemistry. By the use of the balance he proved that whatever the change in matter, the total amount remains the same. He studied combustion and showed that mercury gains in weight when heated in the air. He explained the composition of air and water, gave to hydrogen and oxygen their present names, and advocated the theory of the indestructibility of matter.

Joseph Priestley (1733–1804), an English writer, is generally considered the discoverer of oxygen. He collected gases by mercury displacement, and invented the pneumatic trough. He discovered ammonia, nitrous oxid, and nitric oxid. Priestley was a staunch supporter of the phlogiston theory of combustion. He believed the gas hydrogen to be phlogiston.



27. Combustion. *Ordinary burning is rapid oxidation.* The oxygen combines so rapidly with the burning material that both heat and light are evolved. See Fig. 11. In this chapter we shall think of burning or combustion as rapid oxidation, but later it will be necessary to broaden our definition to include under combustion any chemical action that proceeds so rapidly that light and noticeable heat are



FIG. 11.—A burning oil-tank. The combustion is so rapid that only a part of the carbon is oxidized.

produced. Although Priestley discovered oxygen, the nature of ordinary combustion was first shown by Lavoisier, a French chemist. He had been studying the rusting of metals in air, and, hearing of Priestley's experiments, he came to the conclusion that the "perfect air" described by him was only a very *active* part of ordinary air. He then devised the following classical experiment:

Using an apparatus like that shown in Fig. 12, he heated a weighed quantity of mercury in the retort *r*. The bell-glass *b* contained a definite volume of air confined by the mercury in the dish *d*. During the heating the mercury in the dish rose in the bell-glass showing that the volume of air was being diminished.

At the same time the mercury was being converted into a red powder. After 12 days the action stopped. The mercury in the retort had increased in weight and the volume of air in the bell-glass had shrunk to about four-fifths its original volume. Evidently one-fifth of the air had united with the mercury to form the red powder. When this powder was afterward heated more

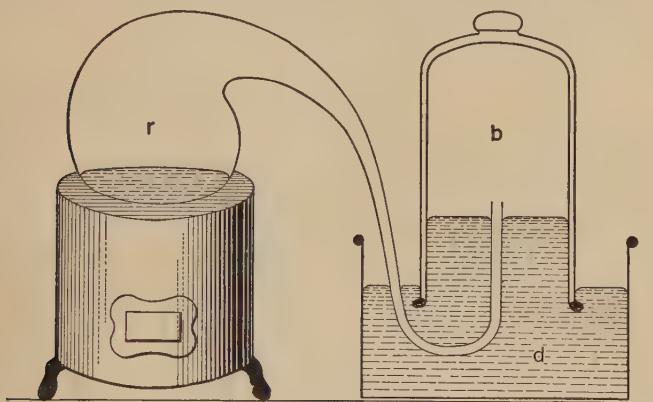


FIG. 12.—Apparatus illustrating method used by Lavoisier to show the nature of combustion.

strongly, a gas was given off which was like Priestley's "perfect air."

Lavoisier named this gas oxygen and proved by his experiment that *ordinary burning is the union of oxygen with some other substance*. Due to this discovery, Lavoisier is commonly called the father of modern chemistry.

Since only about one-fifth of the air is oxygen, substances burn more rapidly in pure oxygen than in air, and some substances that do not burn in air at all, burn vigorously in oxygen. A *glowing* splinter thrust into a bottle of oxygen bursts into flame. This serves as a test for oxygen. Finely divided iron burns in oxygen, giving off dazzling white sparks. Since oxygen is required for ordinary burning, the gas is said to *support combustion*.

28. Kindling Temperature. The furniture of a room is made of combustible material and it is surrounded by air containing oxygen, but it does not take fire. Before wood begins to burn, heat must be applied to raise it to a certain



FIG. 13.—Match (longitudinal section).

temperature. *The lowest temperature at which a substance takes fire, or begins to burn, is called its kindling temperature.*

This temperature varies with the nature of the substance. Phosphorus, for example, has so low a kindling temperature that a slight amount of friction raises its temperature enough to enkindle it. The *head* of a match is made of some material that has a low kindling temperature. When the *head* burns, the chemical reaction is *exothermic*, and enough heat is liberated to enkindle the match-stick. (Fig. 13.)

Since in burning, the oxygen unites with the substance, combustion can occur at the surface only. A match supported as in Fig. 14 in the center of the flame of a Bunsen burner is not enkindled. This shows that such a flame is hollow and that burning occurs only at the surface where the gas comes into contact with the oxygen in the air. This fact may also be shown by momentarily thrusting a sheet of paper down upon the flame. The charred spot on the paper is circular.



FIG. 14.—Match head in flame shows that combustion occurs at the surface only.

It is of interest to study the effect of increasing the surface of a combustible substance. If we split a block of wood, two new surfaces are exposed to the oxygen and combustion is more rapid. If these pieces are split again still more surface is exposed. Wood shavings and paper burn rapidly because they have such large surface areas. A powdered substance

has such an extensive surface that it burns almost instantly, or explosively, if it is loose enough so oxygen can penetrate it readily. *One type of explosion may be defined as practically instantaneous combustion throughout the entire mass.* The carburetor of an automobile mixes gasoline vapor and air in the right proportion for an explosive mixture. In the cylinder of the engine an electric spark ignites the mixture, which burns *explosively*. The hot products of combustion expand forcibly against the piston.

29. Principles Involved in Extinguishing Fires. We have seen that three things are necessary for combustion: (1) *Combustible material*; (2) *a supply of oxygen*; (3) *the substance must be raised to its kindling temperature.* A fire may be extinguished: (1) *by removing the combustible material*; (2) *by shutting off the supply of oxygen*; (3) *by cooling the substance below its kindling temperature.* The successful application of any one of these principles extinguishes the fire. In large city fires, buildings are often dynamited to make the combustible material inaccessible. Water lowers the temperature of the burning substance and as the water evaporates, its vapor shuts off the supply of oxygen. A wet blanket, or a quantity of sand, shuts off the oxygen supply. The effect of lowering the temperature may be seen by holding a copper spiral in a candle flame. The copper conducts the heat away so rapidly that the temperature falls below the kindling point, and the flame is extinguished.

30. Spontaneous Combustion. Several substances oxidize slowly even at the ordinary temperature and some heat is produced. If the air can not circulate freely to disseminate the heat, or if the substance is a very poor conductor, the accumulation of heat may eventually raise the temperature to the kindling point. Thus the substance takes fire spontaneously. Oily rags thrown in a closet and left undisturbed are a source of danger since the slow oxidation of the oil may heat them to their kindling temperature. Fires are

often started in this way by spontaneous combustion. Metal cans should be provided in machine shops for oily waste. Vegetable and animal oils absorb oxygen slowly and may take fire spontaneously. Linseed oil "dries" by the absorption of oxygen, hence rags used by painters are especially dangerous.

31. Products of Combustion. Illuminating gas contains compounds of carbon and hydrogen. As it burns the carbon unites with the oxygen to form carbon dioxid. The hydrogen unites with oxygen forming water. If a beaker of cold water is held in the flame of a Bunsen burner, drops of water formed from the burning hydrogen soon condense on the beaker. The wax of a candle is also composed of carbon and hydrogen. If a short piece of candle is put in a wide-mouthed bottle and lighted, it soon goes out after the bottle is stoppered. Part of the oxygen is used up, and carbon dioxid is produced. A little limewater poured into the bottle becomes milky as the bottle is shaken showing that carbon dioxid was formed by the burning candle. Wood and coal also form water and carbon dioxid when burned. The mineral matter remains as an ash. Since nearly all fuels are made up largely of carbon and hydrogen, the *chief products of ordinary burning are water and carbon dioxid.*

32. Weight Changes in Burning. Lavoisier found that mercury increases in weight when it is converted into the red powder, mercuric oxid. The same is true of all metals that unite with oxygen, such as magnesium, tin, copper, and iron. The increase in weight is evidently due to the weight of the oxygen added.

Wood and coal appear to lose weight when burned. If, however, we weigh both the ash that remains and the gases that are produced, we find that in these cases also there is a decided increase in weight. If we burn a ton of pure charcoal in our furnace, $2\frac{2}{3}$ tons of oxygen will enter the draft of the furnace to combine with the charcoal. By this union $3\frac{2}{3}$ tons of carbon dioxid are formed; the gas escapes up the chimney.

In all chemical reactions, the weight of the factors combining exactly equals the weight of the product or products that are formed. *No weight is ever gained or lost*, a fact that is known as the *grand law of the conservation of matter*.

33. Incombustible Material. It is easy to see why water does not burn if we stop to consider that the hydrogen it contains has already united with all the oxygen it can hold. The same is true with carbon dioxid. Many substances that do not burn are oxids similar in nature to these products of combustion, water and carbon dioxid. For these reasons such substances as calcium oxid, magnesium oxid, and sand (silicon dioxid) make good fireproof materials. Water and carbon dioxid are good fire extinguishers.

34. Relation of Oxygen to Life. Oxygen is one of the most important elements. It may justly be called the life-giving element. Without oxygen animals could live only a few minutes. Taken in through the lungs, it is carried by the hemoglobin of the blood to all parts of the body. It oxidizes a part of our food, thus supplying us with warmth and furnishing us with heat energy. Fishes take oxygen from the air that is dissolved in water. Even plants need oxygen for ordinary respiration. In animal bodies, oxygen slowly oxidizes the waste tissues so they may be readily removed by the organs of excretion. Carbon dioxid and water vapor, waste products of oxidation, are exhaled from the lungs.

35. Decay. Plant and animal tissues contain carbon and hydrogen. These tissues are slowly oxidized in the processes of decay. Several reactions occur, and the presence of bacteria is necessary to bring about these chemical changes. Dry wood does not decay because bacteria grow only on moist surfaces.

36. Uses of Oxygen. 1. *In Special Occupations.* Very often it becomes necessary for a fireman to enter a building filled with smoke, or for a miner to enter a mine filled with poisonous or suffocating gases. Under such circumstances

they make use of an oxygen helmet. See Fig. 15. Oxygen under pressure is carried in cylinders at the back, whence it is supplied through a reducing valve to the breathing bag which is carried on the wearer's chest. Or the oxygen may be generated by chemicals and supplied through a flexible tube to a mask that fits over the nose and mouth of the



FIG. 15.—Self-contained oxygen breathing apparatus.

feet to carry a supply of oxygen. It is also of interest to note that a 420 H. P. Liberty motor develops only 170 H. P. at an elevation of 20,000 feet, because the supply of oxygen is reduced.

2. *For Resuscitation Work.* Pure oxygen is often given to persons suffering from pneumonia and in other cases when

wearer. Figure 16 shows a group of men equipped with oxygen apparatus testing for poisonous gases in a coal-mine. The one at the right has a cage of white mice. These animals and canaries are often used in this way since they are very susceptible to poisonous gases. Divers sometimes are equipped with self-contained oxygen apparatus. The War Department has found that aviators ascending to high altitudes become faint or weakened because the air is too rare to supply enough oxygen. Therefore rules are enforced requiring all aviators flying at a height of more than 10,000

the person is too weak to inhale the necessary volume of air. In cases of asphyxiation from inhaling smoke or other suffocating gases, or from electric shock, a pulmotor or a lungmotor may be used. By means of the lungmotor air rich in oxygen is pumped into the lungs at about the same intervals as in ordinary breathing. In some cases pure oxygen is used.



(Courtesy of Bureau of Mines.)

FIG. 16.—Men equipped with oxygen apparatus used in mines or for rescue work.

See Fig. 17. Care must be taken to prevent injury to the lung tissue by too vigorous use of such apparatus.

3. *For Purification.* Fresh air and sunlight are the best disinfectants. Oxygen in the air is believed to be a very valuable aid in destroying bacteria. Rivers containing sewage are purified in flowing considerable distances by contact with the oxygen in the air. In the sewage disposal

plants of some cities the sewage is sprayed into the air to be purified by the oxygen. Fountains, cascades, and other devices are used to aid in purifying city water supplies. Fig. 18 shows the aëration reservoir at Ashokan where some of the water used to supply New York City is aërated. The water flows 85 miles through an aqueduct 7 feet in diameter.

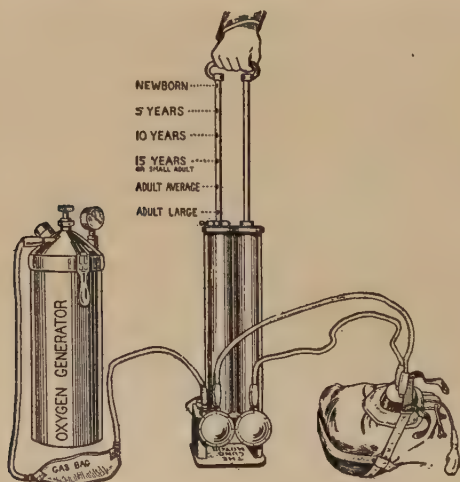


FIG. 17.—The lungmotor is a double action pump used for artificial respiration. The piston stroke may be adjusted to vary the capacity.

4. *For Blowpipe Work.* In 1801 Robert Hare, an American chemist, invented the oxy-hydrogen blowpipe. See Fig. 19. This blowpipe consists of two concentric tubes. Hydrogen from a storage cylinder passes through the outer tube and is lighted at the tip of the blowpipe. The oxygen, passing through the inner tube, combines with the hydrogen and produces a very hot flame. Hare succeeded in melting platinum, sand, aluminum oxid, and other refractory substances. He modestly remarks, "Had I sufficient confidence in my own judgment, I should declare that gold, silver, and

platinum were thrown into a state of ebullition by exposure on carbon to the gaseous flame." The temperature of the oxy-hydrogen flame is estimated to be about 2300°C . It



FIG. 18.—Aëration reservoir for purifying water.

still finds use in melting platinum and quartz and in the fusion of aluminum oxid for making artificial rubies. Drummond produced the *lime light* by directing the flame from such a blowpipe against a stick of lime. The lime does not melt, but it is heated white hot. Any substance thus heated until it *glows* is said to be *incandescent*. Before the advent of the electric arc, the lime light was much used for stage illumination and for stereopticon work.



FIG. 19.—Oxy-hydrogen blow-pipe.

The oxy-acetylene blowpipe, Fig. 20, has largely taken the place of the oxy-hydrogen blowpipe. It gives a much hotter flame, estimated at from 3400 to 3700°C . This blowpipe is

extensively used for cutting metals. See Fig. 21. A similar blowpipe is used for welding metals.

37. Ozone. It is not unusual in chemistry for the same element to exist in two or more different forms. Such an element seems to have a dual personality. Each form is called an *allotropic* modification of the other. Under certain circumstances oxygen may gain energy and form *ozone*, its *allotrope*.

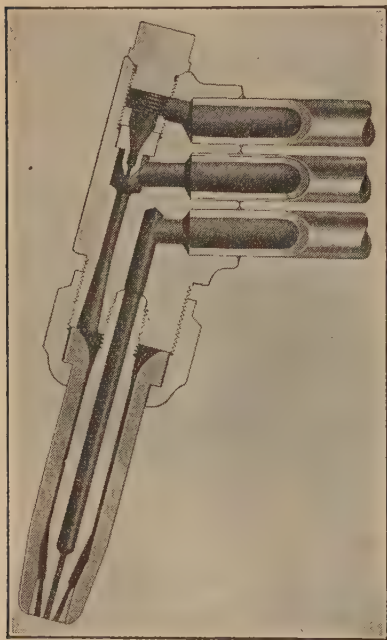


FIG. 20.—Oxy-acetylene blowpipe head.

Some ozone is formed in the air by the lightning during an electrical storm. It may be made by passing electrical sparks through the air, or by the action of the silent "brush discharge." In the ozonizer shown in Fig. 22 the tubes are covered with layers of tin foil. The inner layer is then connected with one terminal of an induction coil and the outer layer to the other

terminal. A small percentage of the oxygen passing through the tube is changed to ozone as it absorbs energy from the electrical discharge.

Ozone has an irritating odor. It is heavier than oxygen and considerably more soluble in water. It is much more active at the ordinary temperature than oxygen. It attacks silver and mercury forming black oxids of these metals. Bacteria are readily destroyed by ozone. It is one of the most

vigorous oxidizing agents known. It causes many colors to fade very rapidly. At a high temperature it is converted into oxygen.

Ozone has been used for bleaching wood pulp, textile fibers, oils, and waxes. In several European cities, Lille, Paris, and



FIG. 21.—Cutting through 12-in. armor plate with the oxy-acetylene flame.

Leningrad, ozone is used to purify water in the city reservoirs. It has the advantage over other bleaching and disinfecting agents of leaving no injurious products, since only oxygen remains. Attempts have been made to use it with ventilating systems. If used in large enough quantities to destroy bacteria, it is irritating to human beings. In smaller quantities

it seems to be successful in eliminating odors, as in slaughter-houses, cold storage rooms, restaurants, and kitchens. So-

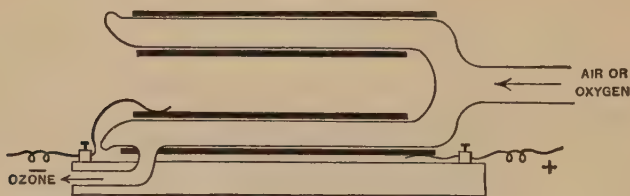


FIG. 22.—Ozonizer.

called “electrified water” is being sold in some localities. Such water has been treated with ozone.

SUMMARY

Oxygen is prepared commercially from *liquid air* or by the *electrolysis of water*. In the laboratory it is usually prepared by heating a mixture of *potassium chlorate* and *manganese dioxid*.

Oxygen is a colorless, odorless, tasteless gas. It is slightly soluble in water. One liter of oxygen weighs 1.43 grams. Oxygen is one of the most active elements, especially at high temperatures.

A *catalytic agent* is a substance that aids chemical action without being permanently changed itself.

The process by which oxygen unites with some other substance is called *oxidation*. The compound furnishing the oxygen is the *oxidizing agent*. The substance upon which the oxygen acts is *oxidized*. The product formed is usually an *oxid*.

Ordinary combustion is rapid oxidation. Before a substance unites with oxygen so rapidly that light and heat are produced it must be heated to a point called its *kindling temperature*.

Three things are needed for combustion: (1) *combustible material*; (2) *a supply of oxygen*; (3) *the material must be heated to its kindling temperature*. Fires are extinguished by eliminating any one of the above factors.

Substances increase in weight when burned on account of the addition of oxygen.

Water and carbon dioxid are products of ordinary combustion.

Ozone is a very active form of oxygen.

QUESTIONS

1. Why would fishes die if put in an aquarium of water which had been heated to the boiling point and subsequently cooled?
2. What changes would occur in nature if the air were pure oxygen?
3. What products are formed by burning tin, copper, phosphorus, magnesium, iron, and sulfur?
4. Paper, wood, and coal are usually added successively when starting a hard coal fire. Explain.
5. When one end of a splinter is thrust into a flame, why does it not burn throughout its entire length as soon as it is kindled?
6. Why are manufacturers especially interested in catalytic agents?
7. Why does a book or magazine burn so slowly?
8. Why is a candle extinguished by blowing? Why does blowing a fire cause it to burn more vigorously?
9. Since powdering a substance makes it burn more rapidly, why is it so difficult to burn coal dust in a furnace?
10. Which should you use to put out a gasoline fire, water or sand? Why?
11. Baking soda gives off carbon dioxide when heated. Is it suitable for use in fire extinguishers?
12. Pyrene fire extinguishers contain carbon tetrachloride, a volatile liquid whose vapor does not burn. Explain how it puts out a fire.
13. Sir Walter Raleigh is said to have made a wager with Queen Elizabeth that he could tell the weight of smoke. He weighed a pipe filled with tobacco, smoked it, and then weighed it again. He gave the difference as the weight of the smoke. Was he correct?
14. Do you think that oxygen would burn in an atmosphere of illuminating gas?
15. When a paint hardens, the linseed oil absorbs oxygen from the air forming a tough, resinous skin. What kind of a chemical would you add to the paint to make it "dry" faster?
16. Why is no ash formed when fuel gas burns?
17. Automobile shops frequently use oxygen. For what purpose?
18. Cork for use in making linoleum is ground between stones to a very fine dust. If the cork is not supplied to the revolving stones continuously, an explosion may occur. Explain.

19. Why should wood and such metals as iron be kept well-painted?

20. What would you do if your clothing caught fire?

PROBLEMS

1. If water is 88.88% oxygen, how many liters of oxygen can be prepared from 100 gm. of water by electrolysis?

2. How many grams of oxygen can be obtained from 5 gm. of potassium chlorate, which is 39% oxygen? How many liters would the oxygen occupy at standard temperature and pressure?

3. Suppose you burn 10 tons of coal during the winter. If that coal is 80% carbon, how many tons of carbon dioxide gas will go up your chimney?

4. Suppose the coal in Problem 3 contains 4% of hydrogen. How many gallons of water would be formed by its complete combustion? (A gallon of water weighs about 8 lb.) Hint. The hydrogen in water is only 11.11% of the total weight.

CHAPTER V

HYDROGEN

38. Occurrence. Although hydrogen is not an abundant element, yet it is very widely distributed. As early as 1766 Cavendish found that a gas was set free when acids act on metals. Later he found that the same gas in burning combines with oxygen to form water. The name *hydrogen* (water producer) was given to this element in 1783 by Lavoisier. Hydrogen is present in all plant and animal tissues. Water is one-ninth hydrogen by weight, and all acids contain hydrogen.

39. Preparation. Of the several ways of preparing hydrogen, only three are given here:

1. *From Water.* (*By Electrolysis.*) This is a commercial method of preparing hydrogen used extensively in the United States and Germany. In our study of oxygen we learned that water is decomposed when an electric current is passed through it. The oxygen is collected at the positive terminal, and the hydrogen at the negative. The hydrogen, which we may consider a by-product in the preparation of

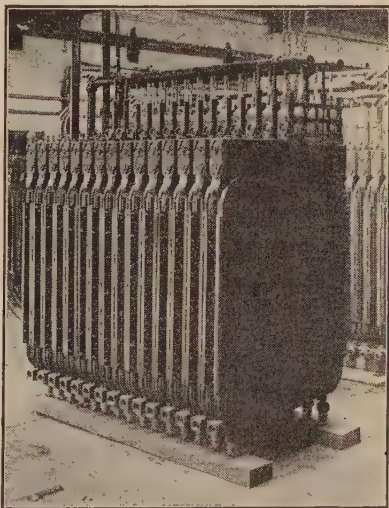
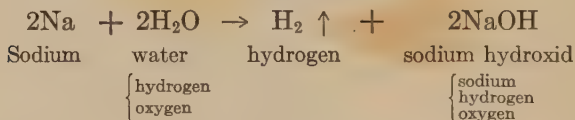


FIG. 23.—Electrolytic cells used for making hydrogen and oxygen.

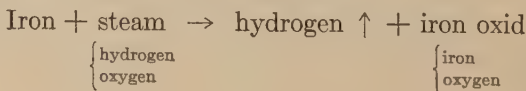
oxygen, is stored in strong steel cylinders under high pressure. Fig. 23 shows a group of cells used for the electrolysis of water.

2. *From Water. (By Action of Metals.)* When we throw a piece of sodium, which is a light, soft, active metal, on the surface of a dish of water, the sodium melts and skims around over the surface. A gas is liberated with a slight hissing sound, and the sodium gradually disappears. The gas, which is hydrogen, comes from the water. The sodium combines with the oxygen of the water and one-half of its hydrogen, but *substitutes itself for* or *displaces* the other half. When the excess water is evaporated to dryness, a white caustic solid, sodium hydroxid (concentrated lye) is left in the bottom of the dish. The following equation shows that the chemical reaction is one of substitution:



Potassium interacts with water even more energetically. The heat which is evolved is sufficient to enkindle the hydrogen, which burns as fast as it is set free from the water. Calcium, however, interacts more slowly than sodium.

Magnesium decomposes boiling water slowly. Iron is another metal that may displace hydrogen from water, but only at a high temperature: When steam is passed through a tube containing finely divided iron that is being strongly heated, the oxygen of the steam combines with the iron and hydrogen is liberated. This method has been used to prepare hydrogen on a commercial scale. The word equation representing the reaction is as follows:



3. *From Acids, by Substitution.* (Usual laboratory method.) All acids contain hydrogen, which may be set free by certain metals. Several different acids may be used, and any one of quite a number of metals. Sulfuric acid is a heavy oily liquid. If we add one part of this *concentrated* acid to five or six parts of water, the *dilute* acid thus formed will attack zinc or iron vigorously. The speed at which the hydrogen is evolved depends upon the amount of surface the metal exposes, the temperature, the strength of the acid solution, and the kind of metal used and its purity.

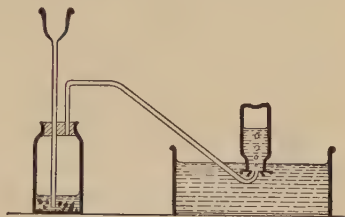
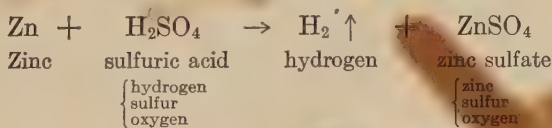


FIG. 24.—Hydrogen generator.

Pure zinc interacts very slowly. In ordinary commercial zinc there is generally enough carbon present to accelerate the action. Fig. 24 shows one type of apparatus commonly used in the laboratory for the preparation of hydrogen. Zinc is put in the bottle and either sulfuric or hydrochloric acid is added through the thistle tube. The hydrogen is collected by water displacement. The action is as follows:



It is customary to say that the metal *dissolves* in the acid, but the statement is incorrect. In reality, the metal interacts with the acid, liberating hydrogen as a gas, and forming a salt, zinc sulfate, which dissolves in the excess water. The metal loses its properties, but it also destroys the acid. One often hears a plumber when making a soldering fluid speak of adding zinc to muriatic acid to “kill” the acid. Zinc sulfate may be recovered as a white crystalline salt from the solution

left in the hydrogen generator by evaporating the excess liquid.

40. Physical Properties. Hydrogen is a colorless, odorless, tasteless gas. It is the lightest gas known, being only one-fourteenth as heavy as air. One liter at standard conditions weighs almost 0.09 gm. Hydrogen is less soluble in water than oxygen.

In 1898 Dewar succeeded in liquefying hydrogen by reducing the gas to a very low temperature and subjecting it to a high pressure. Liquid hydrogen is clear and colorless, only one-fourteenth as heavy as water. Its boiling point is -252.5°C . When a part of the liquid is evaporated rapidly, the remainder freezes to an ice-like solid.

Liquids and gases have the property of intermingling through the pores of membranes. See Fig. 25. This is called

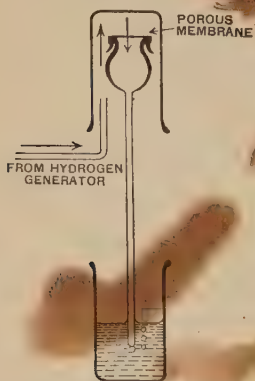


FIG. 25.—Hydrogen readily passes through membranes by osmosis.

osmosis. Hydrogen diffuses in this manner more rapidly than any other gas, since the rate of effusion of gases is inversely proportional to the square roots of their densities. This makes it difficult to keep hydrogen in containers. Rubber balloons filled with hydrogen soon collapse due to the rapid escape of the hydrogen through the pores of the rubber.

Such metals as platinum and palladium absorb hydrogen in large quantities. The absorption of hydrogen in this manner is called *occlusion*. Considerable heat is produced as the absorption occurs, sufficient sometimes to enkindle the gas. Practical use is made of occlusion in the self-lighting gas jets and cigar-lighters.

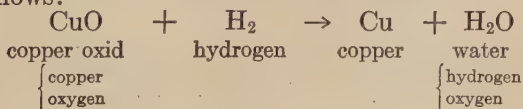
41. Chemical Properties. Hydrogen is not an active element. When oxygen and hydrogen are mixed no chemical action occurs. If the mixture is heated to about 800°C. , or if a flame is brought into contact with it, the mixture explodes violently. Hydrogen and chlorine combine explosively in direct sunlight, forming *hydrogen chlorid*. Under suitable conditions hydrogen combines with nitrogen to form *ammonia*, a very important compound. The Haber process for combining these two elements was put into commercial operation in Germany just a short time before the beginning of the World War. The process will be discussed in a later chapter. Under certain conditions hydrogen has been made to combine with certain metals, forming *hydrides*. Calcium hydride interacts with water, hydrogen being liberated.



FIG. 26.—Hydrogen burns but does not support combustion.

Hydrogen burns with a very hot, pale blue, nearly invisible flame, forming water as its only product of combustion. A blazing splinter thrust into a bottle of hydrogen, as shown in Fig. 26, is extinguished, although the hydrogen catches fire and burns at the mouth of the bottle. This experiment shows that hydrogen does not support combustion.

42. Reduction. In its narrowest sense *reduction* may be defined as the abstraction of oxygen from a compound. If we pass a stream of hydrogen over heated copper oxide, as shown in Fig. 27, the hydrogen unites with the oxygen, forming water, and reduces the copper oxide to metallic copper. The U-tube contains granular calcium chloride which dries the hydrogen gas before it comes into contact with the copper oxide. The equation follows:



It is easy to see that oxidation and reduction are opposite processes. In the above reaction the copper oxid was reduced, while the hydrogen was oxidized; the copper oxid was the oxidizing agent, hydrogen the reducing agent. Oxidation and reduction are very important processes in

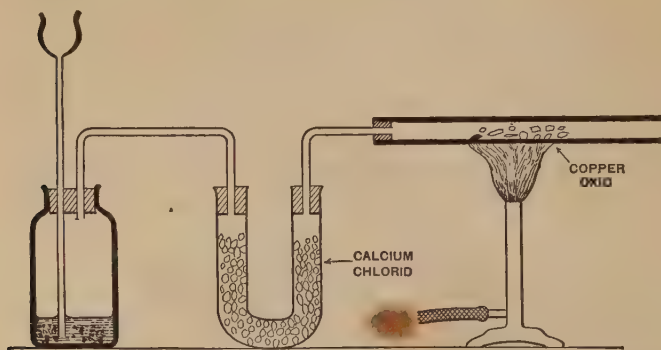


FIG. 27.—Réduction of copper oxid to metallic copper by the use of hydrogen.

chemistry. Often they occur simultaneously, one substance being oxidized as another is reduced.

43. Uses of Hydrogen.

1. *As a Reducing Agent.*—We have just seen that hydrogen is a reducing agent. It is one of the most energetic, since it unites readily with oxygen with the evolution of large quantities of heat. (See Table 8.) Many of our metals are found in nature in combination with oxygen as oxids. To extract the metal the oxygen is often removed by the use of a reducing agent. Hydrogen will reduce the oxids of the *less active* metals, such as copper, tin, lead, zinc, and iron. Carbon, however, is generally used since it is cheaper and more convenient to use. Hydrogen does not reduce the oxids of such *active* metals as aluminum, magnesium, sodium, and potassium. The tungsten used for making filaments for

electric bulbs is swaged and prepared for drawing by heating in a hydrogen furnace to prevent oxidation.

2. *For Its Buoyancy.* Because hydrogen is so much lighter



FIG. 28.—The Los Angeles entering the hangar at Lakehurst. This dirigible is 856 ft. long, 90 ft. in diameter, and almost 102 ft. high. The gas bags hold 2,472,000 cu. ft. of gas. The Los Angeles weighs 91,000 lb., and can carry a load of 88,100 lb.

than air, it is used for filling balloons. Its lifting power per liter is equal to the difference between the weight of 1 liter of air (1.29 grams) and 1 liter of hydrogen (0.09

gram). There are 1000 liters in 1 cubic meter, hence for every cubic meter capacity a balloon's lifting power when filled with hydrogen is 1.2 kilograms, or 2.64 pounds. Military balloons of the Zeppelin type have a capacity of several thousand cubic meters, and can carry several tons. Fig. 28 gives the student some idea of the enormous amount of hydrogen needed to fill a giant dirigible.

3. *As a Fuel.* Hydrogen burns with a flame that is several hundred degrees hotter than that given by the ordinary gas burner. It makes a very good fuel. The water gas, which is now supplied by so many gas companies, contains from 32 to 40% hydrogen. Coal gas and oil gas also contain large quantities of hydrogen, either free or combined with carbon. In the chapter on oxygen we learned that hydrogen is used as a fuel in the oxyhydrogen blowpipe.

4. *For Illumination.* The hydrogen flame is nearly colorless, but it is so hot that it quickly heats a Welsbach mantle to incandescence (page 68). Under such conditions hydrogen is useful for lighting. The Drummond light, or the limelight, which has already been discussed, is another example of the use of hydrogen for illumination.

5. *Hydrogenation of Oils.* Many persons prefer solid fats to oils for cooking purposes. The discovery was made by Sabatier, a Frenchman, that certain oils will combine with hydrogen to form solid fats, if a suitable catalyst (finely divided nickel) is used. Now millions of pounds of cottonseed oil are *hydrogenated* by treating the oil with hydrogen. Crisco is a common cooking fat made by this process. Peanut oil and cocoanut oil are also solidified by this process for use in the making of "nut margarines," or butter substitutes. Certain fish oils, when thus treated, lose their disagreeable odor and become suitable for making soap.

SUMMARY

Hydrogen may be prepared: (1) *by electrolysis*; (2) *by substituting a metal for the hydrogen of water*; (3) *by substituting a metal for the hydrogen of an acid*.

Hydrogen is an odorless, tasteless, colorless gas. It is scarcely soluble in water. It is the lightest gas known. One liter weighs 0.09 gram. Hydrogen burns, but does not support combustion.

Reduction is the process of abstracting oxygen from a compound.

Hydrogen is used extensively as a *fuel*, for *reduction*, for *filling balloons*, and in the *hydrogenation of oils*.

QUESTIONS

1. What precautions should be taken in preparing hydrogen by the usual laboratory method?

2. Would you expect to find hydrogen present in the free state in the air? Give a reason for your answer.

3. Does hydrogen gas make a good fuel? Is it suitable for illuminating purposes?

4. Why is helium being substituted for hydrogen in dirigibles?

5. If there is a blast lamp in your laboratory compare its construction with that of the oxyhydrogen blowpipe. How are they alike?

6. How would you test for hydrogen?

7. Should bottles of hydrogen be kept mouth upward or mouth downward? Explain.

8. Which metal would you use for preparing hydrogen in quantity, zinc or iron? Why?

9. If metallic sodium caught fire, how would you extinguish it?

10. Give two reasons why sodium or potassium is not suitable for preparing large quantities of hydrogen.

11. What would be the effect of lighting the hydrogen at the tip of the delivery tube before all the air had been driven out of a hydrogen generator?

12. Explain what is meant by saying that zinc is added to muriatic acid to "kill" the acid.

PROBLEMS

1. Sulfuric acid is 2.04% hydrogen. How many grams of hydrogen could be prepared from 50 gm. of sulfuric acid?

2. How many liters would the hydrogen gas in Prob. 1 occupy at S. T. P.? How many cubic meters?

3. The Los Angeles holds about 2,472,000 cu. ft. of hydrogen. How many pounds of hydrogen were needed to fill the gas bags?

4. If water is 11.11% hydrogen, how many pounds of water had to be decomposed to supply the hydrogen in Prob. 3?

CHAPTER VI

FUELS—ILLUMINANTS

44. Fuels. The kind of fuel used varies largely with the locality. At one time *wood* was the chief fuel in the United States, but in certain sections wood has become so scarce that coal is used almost exclusively. *Anthracite*, or *hard coal*, is found in quantity in Pennsylvania only; hence high freight rates cause its use to be quite limited, except in the eastern part of the United States. *Soft coal* is found in nearly every state in the Union, therefore it is extensively used for heat and power. *Peat*, *coke*, and *charcoal* are solid fuels that are used more or less commonly.

A few liquid fuels are used to considerable extent. *Kerosene*, *gasoline*, and *alcohol* are clean convenient fuels that are suitable for use in cooking, but too expensive to be used on a larger scale. *Gasoline* and *benzol* are motor fuels. The residues left after the gasoline, kerosene, and lubricating oils have been removed from petroleum are sold as *fuel oils*.

Gaseous fuels have become quite popular. Those used most extensively include *natural gas*, *coal gas*, *water gas*, *producer gas*, *oil gas*, and *acetylene*. They leave no ash and there is no fuel to be handled. Gas is especially desirable for cooking purposes. The heat is concentrated at the point where it is needed. It is so easily enkindled that the gas is ready at any time for instant use, and it is turned off as soon as the meal is cooked. In contrast, starting a coal fire is so difficult that when once started it is kept burning continuously, thus wasting fuel.

45. The Choice of a Fuel. In selecting a fuel, one should inquire what qualities the fuel has that are desirable, and

what qualities are objectionable. The ideal fuel should be low in cost, it should be easily enkindled, and it should have a high heat content. On the other hand, there should be little ash and no waste products that may become a nuisance. Unfortunately, no fuel meets all these conditions. The original cost is apt to be high, and quite often the cost of transportation is more than the original cost. All solid fuels contain mineral matter, which is left as an ash as the fuel burns.

The heat content of a fuel is measured in calories or British Thermal Units. *One calorie is the amount of heat required to raise the temperature of one gram of water one degree Centigrade.* The large Calorie, which is used in dietaries and in tables of food values, is 1000 times as big as the small calorie. The unit used in the English system is the British Thermal Unit (B. T. U.). *The amount of heat needed to raise the temperature of one pound of water one degree Fahrenheit is the British Thermal Unit.* Artificial gas may furnish from 450 to rather more than 600 B. T. U.'s per cu. ft.; one pound of coal generally furnishes from 10,000 to 15,000 B. T. U.'s. If gas furnishes 600 B. T. U.'s per cu. ft., and gas sells at \$1.00 per thousand cu. ft., a man can buy 600,000 heat units of gas for \$1.00. If he pays \$10.00 per ton for coal that gives 12,500 heat units per pound, he buys 2,500,000 heat units for \$1.00. Therefore the choice of a fuel will depend upon the efficiency of the burner and upon convenience, since gas can not compete with coal in price.

Soft coal as a fuel is quite easily enkindled; it does not burn up so rapidly that one must be continually stoking the fire; it has a large number of heat units per pound; it is less costly than many other fuels; the amount of ash is not usually excessive, running from 5 to 10%; its chief defect lies in the fact that dense clouds of black smoke and cinders pour from the chimney when soft coal is burned.

46. Composition of Fuels. Of the fuels named above charcoal and coke are nearly pure carbon. Hard coal is

from 80 to 90% carbon. Soft coal contains slightly less carbon than hard coal. Coal always contains some uncombined or free carbon and a certain percentage of hydrocarbons. A *hydrocarbon* is a compound of carbon and hydrogen.

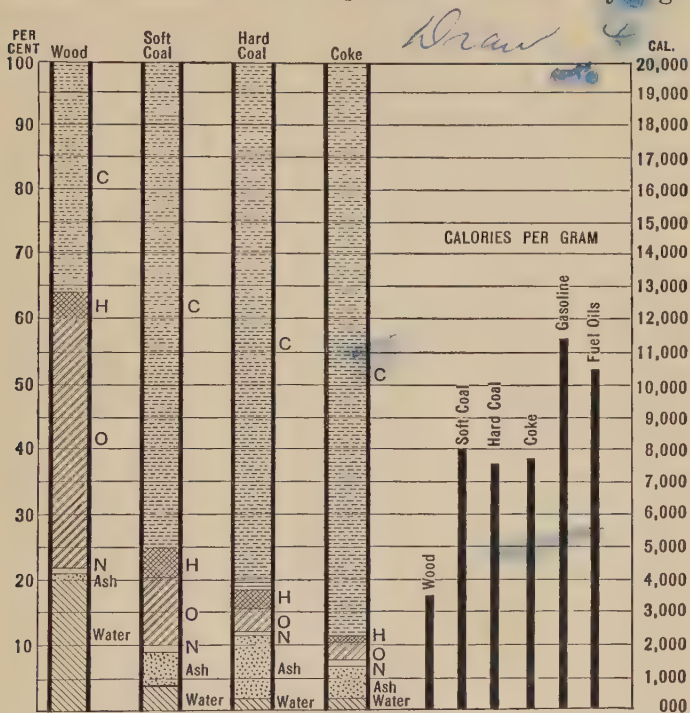


FIG. 29.—Table of fuel composition. Relative heat content of fuels.

Wood is composed largely of cellulose, a compound of carbon, hydrogen, and oxygen. Wood also contains considerable water. Since it requires about 616 calories of heat to change water from room temperature into steam, water in a fuel causes a loss in heat value. The fact has been pretty well established, however, that some water causes a fuel to burn

more readily. Therefore firemen generally add water to coal before it is burned.

The liquid fuels are composed almost entirely of hydrocarbons. Alcohol is an exception, since it contains oxygen, carbon, and hydrogen. When oxygen is present in the fuel itself, the flame is clean and free from smoke, but the heat content of the fuel is lowered.

The gaseous fuels consist largely of hydrogen, hydrocarbons, and carbon monoxid. Fig. 29 shows a more complete composition of several important solid fuels. The heat content of the fuels is also tabulated.

47. Products Formed by the Combustion of Fuels.

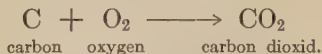
Fuels that contain carbon only, as charcoal and coke, form nothing but oxids of carbon when they are burned. Fuels that contain hydrocarbons form both carbon dioxid and water. It is of interest to note that in hydrocarbons rich in carbon, the supply of oxygen may not be great enough to oxidize both the hydrogen and the carbon. The hydrogen in such cases is oxidized and carbon set free. Sometimes there is only half enough oxygen to unite with the carbon to form carbon dioxid (CO_2). Then the carbon unites with the oxygen to form carbon monoxid (CO), a poisonous gas. Thus we see that an insufficient supply of oxygen causes pollution of the air, either by forming particles of soot or the poisonous gas, carbon monoxid. If we refer to Table 8, in the Appendix, we find that 12 gm. of carbon liberate 97,000 calories of heat when they burn and form carbon dioxid, while the same amount of carbon sets free only 29,000 calories in burning to carbon monoxid. There is a tremendous loss of money when unburned carbon and carbon monoxid escape from chimneys.

48. Furnaces. From a study of Fig. 30, we may get a good idea of the chemistry of fuels. If coal is placed on the grate and enkindled, it is oxidized by the air that enters from beneath through the draft *d*. In starting a fire the damper in the pipe at *b* should be open so the upward current in the

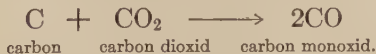
chimney will increase the draft through the grate. After the fire is started, we may close the draft *d* and partly close *b*. Then only a little oxygen comes into contact with the fuel and it burns slowly. It may be made to burn still more slowly, if the check draft *c* is open, since cold air enters and cools the fuel until it may be only slightly above the kindling temperature. Throwing on fresh fuel also cools the fire. If too much is added at one time, the fire may be extinguished by being cooled below the kindling temperature of the fuel.

In a steam heater, part of the water in the boiler is converted into steam which rises to the radiators and gives up its heat to the rooms.

Since coal is largely carbon, the chemistry of its combustion would seem to be the simple oxidation of carbon as follows:



But other reactions may also take place, especially when fresh fuel is added. *Carbon is a reducing agent.* As the carbon dioxid which was formed by the burning of the live coals underneath comes into contact with the carbon of the fresh coal the following partial reduction occurs:



The uncombined carbon from the fresh fuel takes part of the oxygen from the dioxid to form carbon monoxid. If the

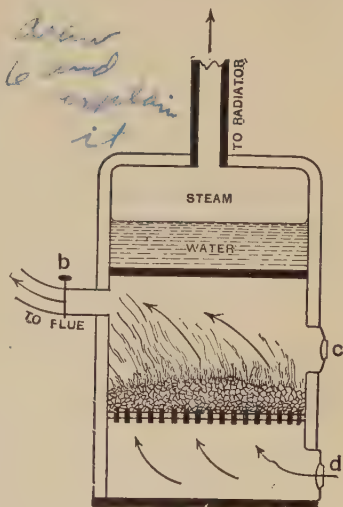


FIG. 30.—Steam heating furnace.

furnace door is left open, this poisonous gas may find its way to the living rooms above. In banking fires at night, the furnace door should never be left open when the damper in the pipe is tightly closed.

49. Smoke. Smoke contains some small particles of very finely divided ash, but its chief constituent is unburned carbon in the form of soot or cinders. Blue smoke from wood contains small drops of liquid hydrocarbons. Soft coal contains so much hydrocarbon that the supply of air is seldom sufficient to oxidize all the carbon. In cities where large quantities of soft coal are used as fuel, the smoke nuisance is almost intolerable. Before efforts were successful in having smoke consumers installed, it was estimated that the smoke nuisance cost the inhabitants of the city of Pittsburgh over \$10,000,000 annually. Estimates place the cost in the United States in waste of fuel, extra laundry work, and other expense at \$500,000,000 annually. This does not include discomfort and injury to health.

50. Smoke Consumers. We have learned that the unburned carbon in smoke is a great nuisance, but it is also very wasteful, since every pound of unburned carbon represents a loss of from 10,000 to 15,000 B. T. U.'s. For these two reasons smoke consumers are now being installed by factories and power plants. The principle of smoke consumption depends upon two things: 1. The fuel should be supplied evenly; 2. The supply of oxygen must be increased to secure *complete* combustion. Fig. 31 shows one type of smoke consumer. It has an *automatic stoking device* to spread the coal evenly on a chain grate. By means of baffle walls the products of combustion are forced to take a circuitous path to the stack or chimney. A large air space is provided so that combustion will be complete. *Supplementary* air is admitted at A, after it has been *preheated* so that it will not cool the flame. Automatic stokers of the rotary type are now in use on many locomotives.

In one type of mechanical stoker the fuel is fed into a large hopper and conveyed under the fire by the sliding bottom of the feed trough that runs the full length of the stoker. As the coal rises in the trough it is distributed over the fire bars. A large volume of air is supplied to the stoker by a blower or fan. Figs. 32 and 33 show a factory before and

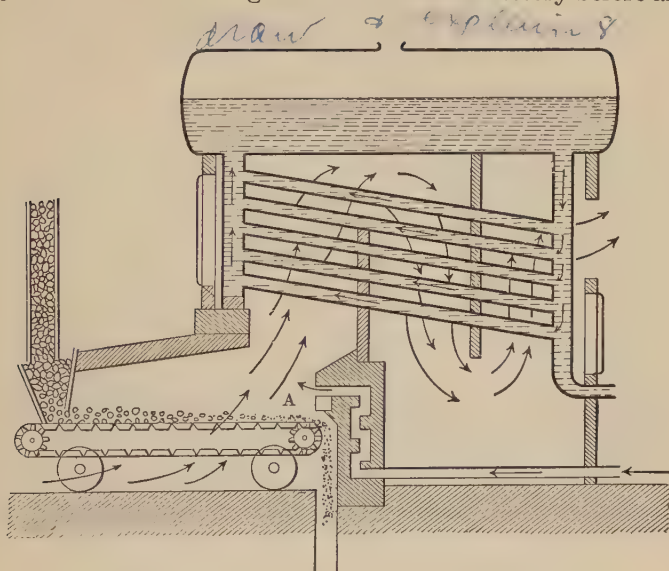


FIG. 31.—Automatic stoker and smoke consumer.

after it was equipped with a mechanical stoker of the under-feed type.

51. Forced Draft. The rate at which a fuel burns depends upon the rapidity with which it is supplied with oxygen. Blowing a fire makes it burn faster for two reasons: (1) the oxygen is furnished more rapidly; (2) the products of combustion are carried away by the draft. A common example of this *forced draft* is the use of a bellows by a blacksmith. The fire burns more rapidly and produces a more

intense heat. It is also interesting to note that fuels burn faster and yield higher temperatures when both the fuel and the air with which it combines are preheated.

On ships forced draft is used when a high speed is desired. More air is forced through the fuel, causing more rapid combustion. The exhaust steam from a locomotive is forced through the smokestack to produce a better draft. A similar effect is produced in power plants by using very tall chimneys. Since the draft of a chimney is caused by the



FIG. 32.—A factory that shows a dirty stack, illustrating the smoke nuisance.

difference in weight between the column of gas inside the chimney and the air-column outside, it is easy to see that this difference becomes greater as the height of the chimney is increased. See Fig. 34. ✓

52. Flame. *A flame is a burning gas.* We are all familiar with the flame produced when a gas is ignited. A candle burns with a flame, but before this flame can be produced, the wax of the candle must be melted and then vaporized. By extinguishing a candle flame, and then quickly bringing a lighted match *near* the wick, the gas that is still being evolved

may be relighted. It is not necessary to touch the wick. Wood and soft coal give off gases when they are heated and burn with considerable flame. Hard coal is not very volatile, therefore it burns with little flame. Coke and charcoal are not volatile, hence they *merely glow*, but produce little or no flame.

53. The Bunsen Burner. The burner shown in Fig. 35 is one of the inventions of Robert Wilhelm Bunsen. This burner consists of the base, the ring, and the tube or barrel.

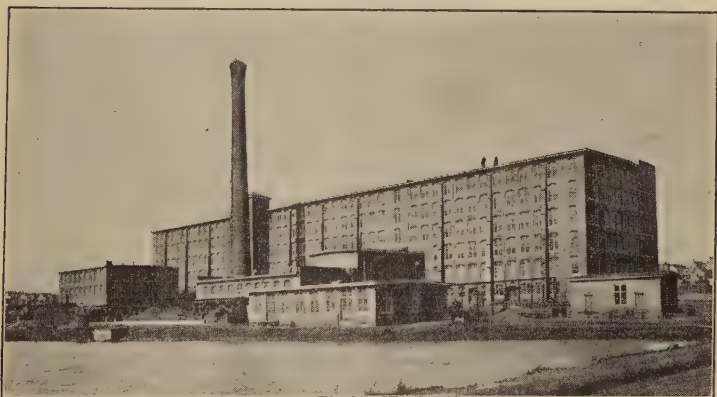


FIG. 33.—The factory shown in Fig. 32 after being equipped with an automatic stoker.

The base has a small tip or spud through which the gas enters the barrel. To secure complete combustion, air enters through the holes at the lower end of the tube and mixes with the gas before it burns at the top of the tube.

The amount of gas that enters the barrel varies with the pressure from the mains and with the size of the opening in the base. The ring is used to regulate the air supply, by opening or closing the holes in the tube. As more gas is used, more air should enter at the lower end of the tube. If the gas is partly turned off, or the pressure is too low, it will burn

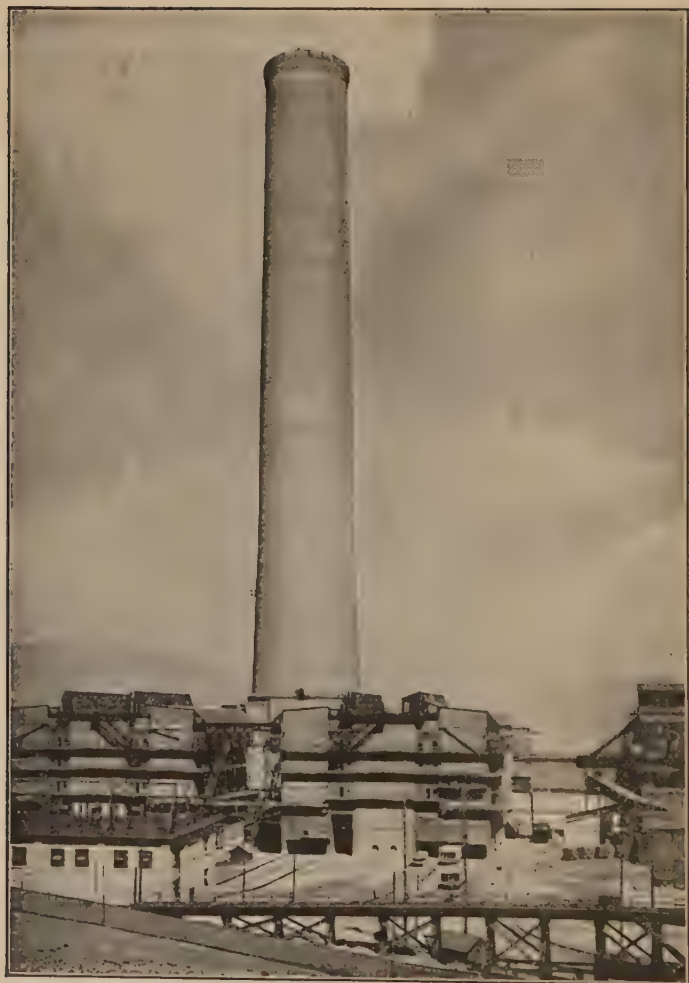


FIG. 34.—This stack built for smelting copper ores in Montana is so large that the Washington Monument would disappear from view if it were placed inside. Its height is 583 feet.

faster than it is supplied at the top of the tube. The relative amount of air increases until an explosive mixture is formed. It then strikes back and burns at the spud. The base then becomes hot and may melt the rubber tubing and set fire

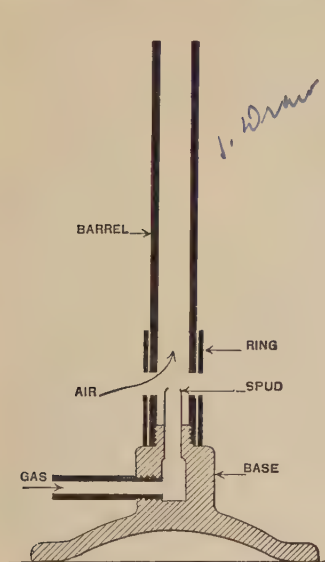


FIG. 35.—Parts of a Bunsen burner longitudinal section.

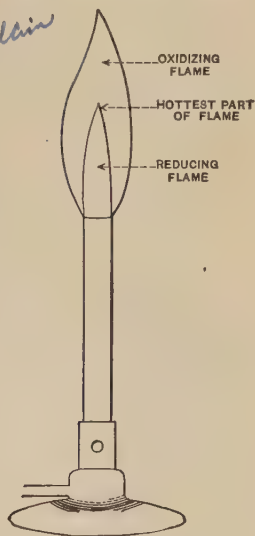


FIG. 36.—Bunsen burner, showing parts of flame.

to the escaping gas. As the gas is turned partly off to lower the flame, the holes should be partly closed.

The flame of the Bunsen burner consists of two distinct cones. The outer cone is called the *oxidizing flame*, since metals held in this flame are soon oxidized. The inner cone is called the *reducing flame*. { Copper oxid held in this cone is reduced to metallic copper. } The tip of the inner cone is the hottest part of the flame. See Fig. 36.

All types of gas burners used for heating are modeled after the Bunsen burner. Even the carburetor is similar in

principle. In this case, however, an explosive mixture is desirable. It is the function of the carburetor to vaporize the gasoline and mix it with enough air to form a mixture that will explode violently in the cylinders of the engine.

54. Luminous and Non-luminous Flames. When the holes of the Bunsen burner are open the flame is nearly colorless and gives very little light. If we close the holes, a yellow luminous flame is produced. A beaker of cold water

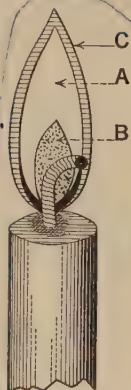


FIG. 37.—Candle flame, showing parts.

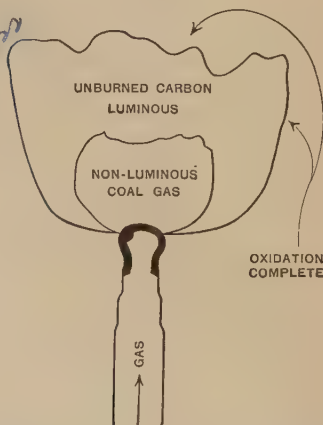


FIG. 38.—Gas jet, fish-tail burner.

held in this flame is soon covered with soot, showing that the combustion of the carbon is incomplete. The light which a candle, a kerosene lamp, or a gas jet gives is due to particles of unburned carbon which are heated to incandescence. This statement may be further verified by opening the holes to produce the hot, nearly colorless flame and then sprinkling particles of iron rust into the flame. The flame becomes luminous as the particles are heated white hot.

55. The Candle Flame. The ordinary candle is made of paraffin, stearin, spermaceti, or other wax or fat. These substances contain carbon and hydrogen. When heated

and enkindled, the melted wax rises by capillarity to the end of the wick where it burns with a rather complex flame. Fig. 37 shows that the flame is made up of three distinct cones. Surrounding the wick is the cone *B*, which consists of unburned gases. In the middle cone *A* the gases become hot enough so that a partial decomposition of the hydrocarbon occurs and some carbon is set free. By being heated to in-

candescence it forms the luminous cone of the candle. In the third cone *C*, which is narrow and almost

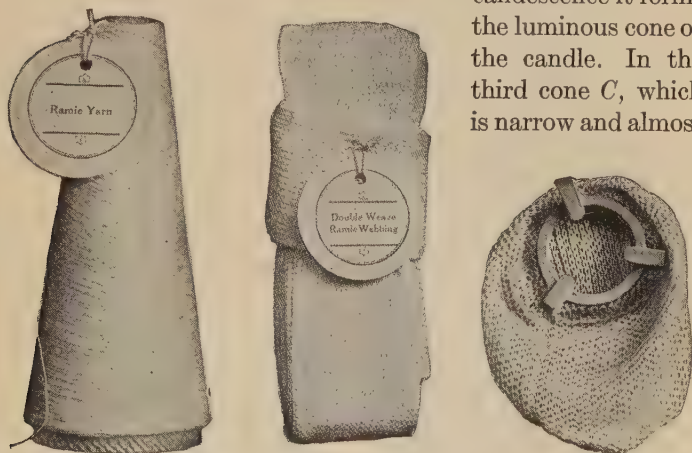


FIG. 39.—Welsbach gas mantles, showing how the fibers are woven and mounted.

invisible, complete combustion occurs, water and carbon dioxid being formed. In making the wicks of modern candles, one thread is drawn more tightly than the others. Thus as the candle burns the end of the wick is pulled to one side and burns in the edge of the flame. In this way it automatically trims itself.

56. The Gas Jet. Fig. 38 shows the ordinary gas jet, or the fish-tail burner. To prevent the gas from burning with a smoky flame, the opening of the jet is a narrow slit. This produces a flat rather than a circular flame and better

oxidation is secured. If too much surface is exposed to the oxygen of the surrounding air, the flame will be non-luminous on account of complete combustion. With a burner of this type there is no mixing of the air and gas before it reaches the tip of the burner.

57. Gas Mantles. To utilize the heating effects of gas for illuminating purposes, a gas mantle is suspended in the flame. The mantle is heated to incandescence. Dr. Auer von Welsbach devised the mantles as shown in Figs. 39 and 40. The mantle is woven from ramie or artificial silk, dipped into

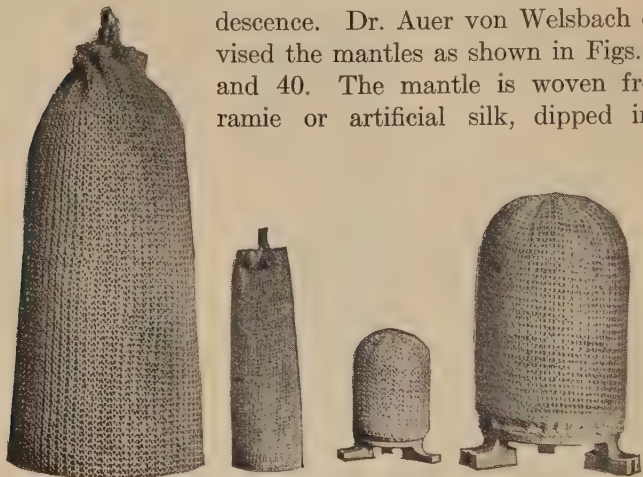


FIG. 40.—Welsbach gas mantles, erect and inverted types.

solutions of the nitrates of cerium and thorium, and then heated to convert these nitrates into oxids. The finished mantle consists of the oxids of cerium and thorium, about 1% of the former to 99% of the latter. The oxids of these rare metals are very refractory, and when heated they give a very fine white light. They are so fragile that they must be covered with a collodion film to prevent breakage during shipment.

58. Acetylene as an Illuminant. The acetylene industry dates from about 1899 when Willson, an American chemist,

was experimenting by heating coke and lime in an electric furnace. Not being successful in obtaining the product he was working for, he dumped the grayish-black residue into a stream at Spray, N. C. An inflammable gas was evolved in quantity. The product he had thrown away in disgust proved to be calcium carbide, a compound which interacts vigorously with water to form acetylene. Acetylene is a hydrocarbon (C_2H_2). Since more than 92% of the compound

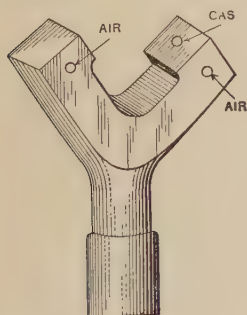


FIG. 41.—Acetylene burner.

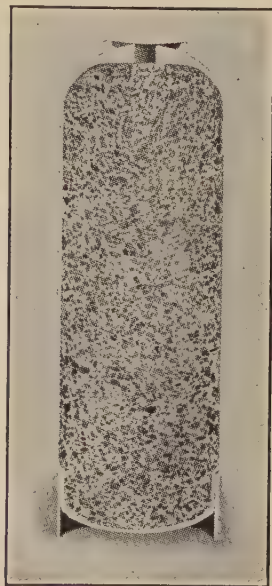


FIG. 42.—Cylinder for storing acetylene.

by weight is carbon, acetylene burns with a smoky flame unless a special burner is used. See Fig. 41. Used with a special burner designed to admit air, acetylene burns with a beautiful white light.

59. Acetylene Beacons. During the last 15 years the use of acetylene in making signaling devices has increased greatly. Many lighthouses use acetylene to flash warning signals. Every three miles along the air-mail route acetylene beacons have been placed to guide aviators. Hundreds of

“silent policemen” are found at street intersections, at railroad crossings, and at the approach to dangerous curves and blind roads.

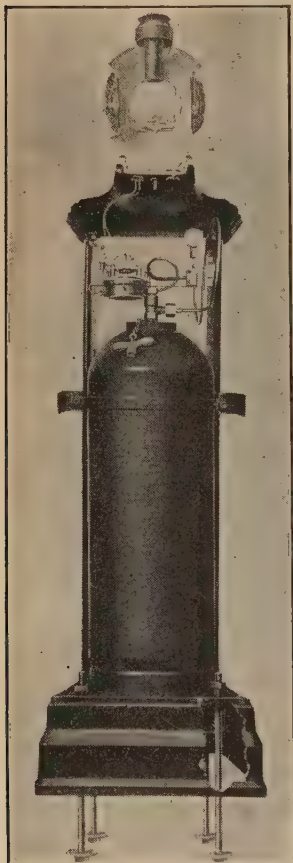


FIG. 43.—The inside mechanism of a “traffic beacon.”

Dalen, a Swedish inventor, was awarded the Nobel prize in physics in 1912 for his work as inventor of the regulating devices which make the intermittent flashing of such beacons automatic. The acetylene is stored in strong steel cylinders which are first packed with a mixture of kieselguhr, charcoal, asbestos, and cement. Acetone is then added to this porous mixture. Under pressure acetylene dissolves in the acetone, escaping again when the pressure is released. Fig. 42 shows a sectional view of such a cylinder.

In the familiar “traffic beacon,” which is shown in Fig. 43, such a cylinder of acetylene is used. The gas flows through a reducing valve which lowers the pressure to about $\frac{3}{4}$ lb. per sq. in. The flow of the gas to the burner is controlled by a permanent magnet which lifts under pressure to let the gas escape. A pilot light at the base of the burner ignites the escaping gas

and produces the intermittent flash. The device is automatic, requiring no attention for six months or more. Lighthouses in the Arctic regions operate without attention

for two years. A sun valve shuts off the gas when the sun shines, but it comes on again automatically when it grows dark. Such lighthouses use a Welsbach mantle, which is also replaced automatically if accidentally broken.

SUMMARY

Any substance that readily combines with oxygen to furnish heat is a fuel. A good fuel should have little ash, a high heat content, should not be expensive, and should not produce undesirable products as it burns.

Fuels, whether solid, liquid, or gaseous, consist largely of *carbon*, *hydrogen*, and sometimes *oxygen*.

The products of complete combustion are carbon dioxide and water. Free carbon and carbon monoxide are formed when the combustion is incomplete.

Smoke consists largely of particles of *unburned carbon*. Smoke consumption is based upon two principles: (1) *to increase the supply of air, thus making the combustion complete*; (2) *to feed the coal to the fire gradually by means of an automatic stoking device*.

A flame is a burning gas.

The flame of the Bunsen burner has two cones: the inner cone is the *reducing* flame; the outer cone, the *oxidizing* flame.

When combustion is complete a flame is usually nearly colorless. The luminosity of the ordinary gas flame is due to particles of unburned carbon heated to incandescence.

A gas mantle is often used to increase the efficiency of the gas flame when used for illumination.

Acetylene gas is a good illuminant. It finds use in lighthouses, railway signals, and traffic beacons.

QUESTIONS

1. Discuss the value of wood as a fuel, using the method outlined in section 45.

2. Discuss the value of hard coal as a fuel. Of fuel oils.

3. Summarize the advantages of gas as a fuel.

4. Why is it dangerous to check a fire by closing the smoke damper and opening the furnace door? Why is opening the furnace door an extravagant method of checking a fire?

5. Why do charcoal and hard coal burn slowly?

6. In the fish-tail burner the gas issues from a narrow slit. Why doesn't the gas burn with a smoky flame?

7. Briquettes are made by compressing coal dust mixed with some tarry material which serves as a binder. What advantage have these lumps as a fuel?

8. How could you determine the per cent of ash in a sample of coal?

9. Under what conditions does gasoline vapor explode?

10. If a kerosene lamp smokes, what are the probable causes?

11. Vessels at sea have used a smoke screen to escape from submarines or other hostile craft. Tell how such a screen can be produced.

12. Why is it dangerous to work in a closed garage with the engine running?

13. Suppose your gas stove "strikes back." How would you adjust the burner? How would you fix the burner of your gas stove if the tips of the small flames were yellow?

14. Is bread a fuel? What do we mean when we say that a thick slice of bread furnishes 100 Calories (100,000 small calories)?

15. Compare the human body with a furnace.

CHAPTER VII

THE GAS LAWS

60. Measurement of Gases. Since it is quite a difficult task to weigh gases, they are usually measured by volume. But we have already learned that the volume changes with a change of temperature or of pressure. Therefore a standard is necessary. Scientists have agreed to use as the standard temperature 0° C., the temperature of melting ice. As the standard pressure the weight of a column of mercury 760 mm. long was chosen. This is equal to a pressure of 1034 gm. per sq. cm., or 14.7 lb. per sq. in.

61. Why 760 mm. was Selected. Every one knows that it is possible to suck soda water through a straw, but not every one knows why the water rises in the straw. A few centuries ago men believed that liquids rise in exhausted tubes because "nature abhors a vacuum." But when the Duke of Tuscany found that water would rise in his pump to a height of only 32 ft., he went to Galileo for an explanation. The answer to the problem was worked out by Galileo's pupil, Torricelli, who reasoned that mercury, being 13 times as heavy as water, would rise only $1/13$ as high (about 30 in.) in an exhausted tube.

Torricelli filled a glass tube about 36 in. long, closed at one end, with mercury and inverted it in a bowl of mercury. See Fig. 44. The mercury in such a tube stands about 30 in., or

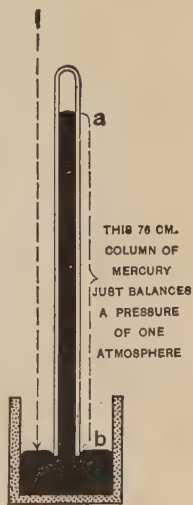


FIG. 44.—Simple barometer.

760 mm., above the level of the mercury in the bowl. Thus Torricelli proved that the pressure of the surrounding air is responsible for the rise of liquids in exhausted tubes, and that this pressure at sea level is just great enough to sustain a column of mercury 760 mm. high. When the air pressure increases, more mercury is forced up the tube. Part of the mercury flows out when the air pressure is reduced. "760 mm. of mercury" was chosen as standard pressure because the atmosphere at sea level just balances a column of mercury of that height. Since we live at the bottom of an "ocean of air," we are under the same pressure as if we lived under 34 ft. of water or 760 mm. of mercury.

62. The Barometer. A simple barometer consists of a Torricellian tube which has been fitted with a graduated



scale so that the height of the mercury can be easily measured. Of course the height of the mercury column will vary as the pressure of the air changes slightly from day to day. The student must remember as he works with gases in the laboratory that a bottle of gas is at all times under pressure due to the atmosphere. Fig. 45 shows that a bottle of gas standing on the laboratory desk really sustains a pressure equivalent to that of the air pressure. For exact measurement at a given time one has merely to read the barometer.

FIG. 45.—The gas in an open bottle is under a pressure equal to that of the atmosphere.

63. Effect of Pressure on Volume.

Suppose we have a bottle of 1000 c. c. capacity. If we fill this bottle with hydrogen gas at 0°C. , and put it under a pressure of 760 mm. of mercury, the weight of the contained hydrogen is approximately 0.09 gm. If we increase the pressure, the volume will be reduced.

Robert Boyle, in experimenting with gases, found that the volume of a gas decreases as the pressure upon it is increased. If a gas has a volume of 1000 c. c. when the pressure upon it is 760 mm., its volume will be only 500 c. c., or one-half its original volume, if the pressure is doubled. Tripling the pressure reduces the volume to one-third the original volume. Conversely, reducing the pressure causes the volume to expand. These facts were concisely stated by Boyle in the following law which bears his name: *If the temperature remains constant, the volume of a confined gas is inversely proportional to the pressure it sustains.*

64. Effect of Pressure on Density. *The density of a substance may be defined as its weight per unit volume.* Since 1 c. c. of copper weighs 8.8 gm., we say that the density of copper is 8.8 gm. per c. c. 1 cu. ft. of water weighs 62.4 lb.; hence in the English system we express density in pounds per cu. ft.

Expressed mathematically, density = $\frac{\text{weight}}{\text{volume}}$.

When an increased pressure reduces the volume of a gas, its weight is not changed. Therefore, its density must have increased. In all cases, if the temperature remains constant, *the density of a gas is directly proportional to the pressure it sustains.* A box that holds 0.5 gm. of a given gas under a pressure of one atmosphere will hold 2 gm. under a pressure of four atmospheres.

PROBLEM: A 1000 c. c. bottle is filled with hydrogen gas when the barometer reads 745 mm. What volume will the gas occupy at standard pressure, or 760 mm.?

SOLUTION: Since the pressure is increased from 745 mm. to 760 mm., the volume will be reduced to $745/760$ of its original volume. $745/760$ of 1000 c. c. equals 980.2 c. c., the volume at standard pressure.

Or, substituting in the formula, $VP = V' P'$, in which V and P represent respectively the original volume and pressure and V' and

P' the new volume and pressure, we get $1000 \times 745 = V' \times 760$. Whence, V' equals 980.2 c. c.

65. Boyle's Law Shown Graphically. The curve of Fig. 46 shows how a given volume of gas, 2,000 c. c., at a pressure of 200 mm., behaves when subjected to the various pressures recorded along the margin of the curve. On a sheet of squared paper, we measure volumes from a certain horizontal

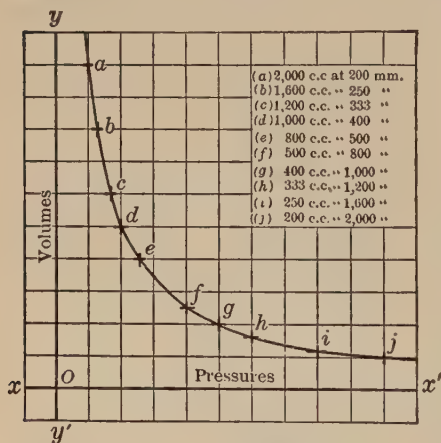


FIG. 46.—Curve of inverse proportion.

line, XX' . From the vertical line YY' as a base we measure pressures. The point of intersection of the two axes is taken as the origin of the curve. Suppose we let one small space represent 200 units. The first volume is 2000, which will be 10 spaces from the XX' axis; the corresponding pressure is 200 units, which is

one space from the vertical axis YY' . This gives us the point a . In a similar manner we find the point b , using 1600 and 250 as units. By using each pair of coördinates in turn, we locate the other points of the curve. By tracing a smooth line through all these points, we have a *curve of inverse proportion*. In all cases, we find that $VP = a \text{ constant}$. A little practice makes it easy to interpret laws from curves. For example, we observe that as the pressure is increased the point locating the curve is nearer to XX' , but farther from YY' .

66. Effect of Temperature on Gas Volumes. When gases are heated they expand. This is also true of liquids and

solids, but the expansion per degree change in temperature is not so great. For example, mercury expands nearly 7 times as much as glass, but any gas will expand nearly 20 times as much as mercury. Every one is familiar with the increase in volume of the gases from baking powder when biscuits are put into a hot oven. Charles, a Frenchman, found that *all gases have the same coefficient of expansion*. If the pressure does not change, a gas at 0°C . will expand $1/273$ of its volume when heated to 1°C . If heated to 100°C ., its volume will be increased by $100/273$, or it will have a volume equal to $373/273$ of its original volume; heated to 273°C ., its volume will be doubled.

If a gas at 0°C . be cooled to -100°C . its volume will be reduced to $173/273$ its original volume. Cooling to -200°C . reduces the volume to $73/273$. At -273°C . the gas would theoretically have no volume. In practice all gases liquefy before that temperature is reached.

67. Absolute Temperature. Theoretically if a gas were cooled to -273°C . and its volume reduced to zero, all molecular motion would cease, and the substance would be

C.	A.	Vol.
100	373	373
50	323	323
20	293	293
0	273	273
-100	173	173
-273	0	0

FIG. 47—Comparison of Absolute and Centigrade scales.

absolutely without heat or at *absolute zero*. For this reason -273°C . equals 0°A ., or zero on the absolute scale. Fig. 47 shows a comparison of the Centigrade and Absolute scales of temperature and also gives the corresponding volume changes in a gas that measures 273 c. c. at 0°C . The law of

Charles may be stated as follows: *If the pressure is constant, the volume of a gas is directly proportional to the absolute temperature.* We convert Centigrade temperatures to Absolute temperatures by adding 273° to the Centigrade reading. The Absolute scale is never used for measuring temperatures. It is merely an arbitrary scale devised to eliminate the zero and the minus from the regular thermometer scales. It is easy to work problems by proportion by the use of the Absolute scale since all the readings are plus. On the other hand, it would be impossible to find any proportional volume relations between a gas measured at 10° C. and one measured at -10° C.

PROBLEM: Given 500 c. c. of a gas measured when the temperature is -10° C. What volume will the gas occupy at 10° C.?

SOLUTION: -10° C. = 263° A.; 10° C. = 283° A. Since the gas was warmed from 263° A. to 283° A., its volume will expand to $283/263$ of its original volume. $283/263$ of 500 c. c. = 538.0 c. c., the new volume.

Or, we may substitute in the following formula: $V : V' = T : T'$. $500 : V' = 263 : 283$. Whence, $V' = 538.0$ c. c. Of course T and T' represent absolute temperatures.

68. Law of Charles Shown Graphically. Fig. 48 shows a *curve of direct proportion* which represents the changes in volume a gas undergoes when heated. The absolute temperatures and volumes shown in Fig. 47 were used as coordinates in plotting this curve. The curve shows clearly that as one factor is increased the other is correspondingly increased.

Suppose we plot the curve AB , Fig. 49, using the volumes shown in Fig. 47 as abscissas, and the *Centigrade* temperatures as ordinates. If we produce the curve backward it will intersect the YY' axis at Z , a point equivalent to -273° C., or to zero degrees Absolute. This furnishes a graphic illustration of the theoretical temperature at which all gases cease to have volume. A study of the figure also shows why

Absolute temperatures rather than Centigrade must be used in solving problems involving the use of the law of Charles. In the similar triangles ZCD and ZOA , we observe that $OZ : CZ = OA : CD$. Therefore OA and CD , the corresponding volumes, are proportional to OZ and CZ , the

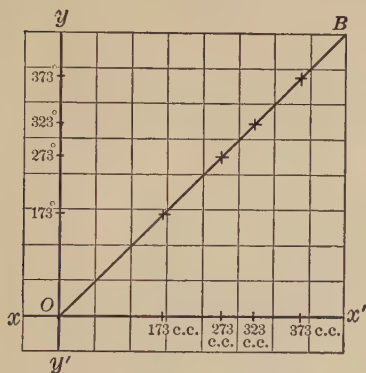


FIG. 48.—Curve to represent law of Charles.

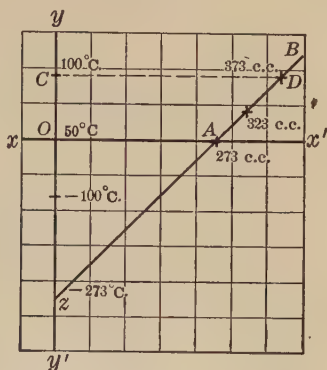


FIG. 49.—Curve to show absolute zero.

absolute temperatures. They are *not* proportional to the Centigrade temperatures.

69. Correction of Volumes When Both Temperature and Pressure Change. Problems involving both temperature and pressure changes are very common. In solving such problems, it is possible to find the effect of pressure alone and then use that volume to find the effect of temperature. It is even simpler to combine both changes in one mathematical statement.

PROBLEM: Given 500 c. c. of gas measured at 20°C . and 750 mm. pressure; find what volume the gas will occupy at 30°C . and 760 mm. pressure.

SOLUTION: $20^{\circ}\text{C} = 293^{\circ}\text{A}$.; $30^{\circ}\text{C} = 303^{\circ}\text{A}$.

Then, $500 \times 303/293 =$ the volume corrected for temperature only.

And, $500 \times 750/760 =$ the volume corrected for pressure only.

Since both the temperature change and the pressure change occur simultaneously, we may combine the equations as follows:

$$500 \times 303/293 \times 750/760 = \text{corrected volume.}$$

Note. The increase in temperature from 20° C. to 30° C. causes the gas to expand by 303/293 of its volume, and the increase in pressure reduces its volume by 750/760.

The following formula may be used in solving problems of this type: $\frac{PV}{T} = \frac{P'V'}{T'}$. In this formula, P , V , and T represent the original pressure, volume, and absolute temperature respectively; P' , V' , and T' represent the new pressure, volume, and absolute temperature.

70. Corrections for Barometer Readings. 1. *When levels can not be adjusted.* In collecting gases by liquid displacement, it is customary to adjust the levels if the volume of the gas is to be measured. Sometimes this is impossible, and

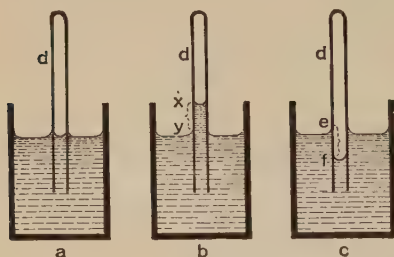


FIG. 50.—Difference of levels.

then the reading of the barometer must be corrected. In Fig. 50*a*, the liquid in the tube stands at the same height as that outside. Therefore the gas d is exerting the same pressure that the air does outside. We know that the pressure

which the gas sustains can be found by reading the barometer, and that no correction is necessary.

If we refer to Fig. 50*b*, we see that the pressure which the gas d sustains is less than the barometer reading, for it requires the gas pressure plus the weight of the column of liquid xy to equal the pressure outside. Suppose the gas is collected over mercury and xy is 60 mm. high. If the barometer reads 740 mm., then the gas pressure of d plus 60 mm. = 740 mm. The gas d alone exerts a pressure of 740 mm. — 60 mm., or 680 mm. In solving any problem for change in

pressure on this gas, we would use as the original pressure 680 mm. If the gas had been collected over water and *xy* were a water column 68 mm. long, then we would not have *subtracted* 68 mm. from the barometer reading, but 68 divided by 13.6, since mercury is 13.6 times as heavy as water. The *true* pressure of the gas in such case would be 735 mm. $(740 - \frac{68}{13.6})$.

In Fig. 50c the gas *d* exerts a pressure greater than that of the atmosphere by a column of liquid *ef*. In this case the reading as shown by the barometer must be corrected by *adding* as many millimeters as *ef* measures, if the liquid is mercury, or the number of millimeters divided by 13.6, if the liquid is water. To find the correct pressure the gas exerts when the inside level is the *higher* of the two we must *subtract* from the barometer reading the length of the column *xy* if the liquid used is mercury. If the inside level is *lower* than the outside one, we must *add* to the barometer reading the length of the column *ef* as a correction. If the liquid used is *water* as is usually the case, the length of the water column divided by 13.6 (since mercury is 13.6 times as heavy as water) must be *subtracted* from or *added* to the barometer reading as above.

PROBLEM: A gas collected over mercury measures 40 c. c. when the mercury stands 90 mm. higher in the tube than outside; the temperature is 18° C., and the barometer reading 755 mm. What volume will the gas occupy at standard temperature and pressure?

SOLUTION: The barometer reading corrected for difference of levels equals 755 mm. less 90 mm., or 665 mm. This is the real pressure upon the gas. The corrected volume is then found as follows: $40 \text{ c. c.} \times 273/291 \times 665/760 = 32.8 \text{ c. c.}$

2. *When the Gas Contains Water Vapor.* When gases are collected over water, they will be moist because water has been evaporating at the same time. After a time the gas standing above the water becomes saturated with water vapor. The amount of water vapor needed to saturate a gas

depends upon the temperature. See Table 3 in the Appendix. When evaporation occurs in this manner, the vapor exerts

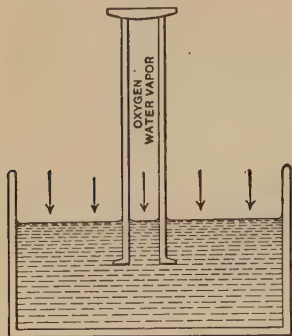


FIG. 51.—The combined pressure of the oxygen and water vapor equals the pressure of the atmosphere.

from the barometer reading the pressure which the water vapor exerts.

a pressure upon the liquid. Suppose we let a bottle of oxygen gas stand over water as in Fig. 51 until it is saturated with water vapor. Suppose the temperature is 26°C . and the barometer reads 775 mm. The pressure of the oxygen gas plus the pressure of the water vapor (25 mm. as shown in Table 3) equal 775 mm. The pressure of the oxygen alone is equal to 775 mm. — 25 mm., or 750 mm. Therefore, if we wish to find the volume of a *dry* gas we must always *subtract*

PROBLEM: Four hundred c. c. of oxygen are collected over water. The temperature is 20°C ., and the barometer reads 750 mm. Find what volume the *dry* oxygen will have at standard temperature and pressure.

SOLUTION: From the table we find that at 20°C ., water vapor exerts a pressure equal to 17.4 mm. of mercury. Then the oxygen gas alone is exerting a pressure of 750 less 17.4 mm., or 732.6 mm. This part of the operation is generally spoken of as correcting the barometer reading for pressure due to water vapor. The volume of oxygen at standard conditions may now be found by using the following equation: $400\text{ c. c.} \times 732.6/760 \times 273/293 = 359\text{ c. c.}$, the corrected volume.

Very often a correction for both aqueous pressure and difference of levels is necessary as in the following problem:

PROBLEM: A gas collected in a tube over water measures 75 c. c. when the outside level is 68 mm. higher than the inner; the temper-

ature is 20°C . and the barometer reads 757.4 mm. Find the volume of the *dry* gas at standard temperature and pressure.

SOLUTION: The barometer reading corrected for aqueous pressure equals 757.4 mm. — 17.4 mm., or 740 mm. The correction to be *added* for difference of levels is 68/13.6, or 5 mm. The *true* pressure of the gas is 740 mm. plus 5 mm., or 745 mm. Solving by the use of the laws of Boyle and Charles,

$75\text{ c. c.} \times 745/760 \times 273/293 = \text{new volume.}$ The result is 69.2 c. c.

SUMMARY

Gases *expand* when heated and *contract* upon cooling. *Increasing* the pressure upon a gas *reduces* its volume. The *standard temperature* for measuring gases is 0°C .; the *standard pressure* is 760 mm. of mercury.

The volume of a dry gas is *inversely* proportional to the pressure it sustains. This statement is known as the Law of Boyle, which may be stated algebraically as follows: $VP = V'P'$, or $VP = a \text{ constant}$.

Charles found that the volume of a gas is *directly* proportional to the *absolute* temperature. The law may be stated as follows: $V : V' = T : T'$.

The following formula may be used to find the volume of a gas when both the temperature and pressure change: $\frac{VP}{T} = \frac{V'P'}{T'}$.

This expression is often called the "Gas Law."

To convert Centigrade temperatures to Absolute temperatures add 273° to the observed temperature on the Centigrade scale.

PROBLEMS

1. A gas collected when the pressure is 820 mm. has a volume of 2000 c. c. Find its volume at standard pressure.

2. A gas has a volume of 100 c. c. when the pressure is 65 cm. What pressure will be needed to reduce the gas volume to 60 c. c.?

3. A liter vessel was filled with gas when the barometer read 780 mm. What will be the new volume of the gas if the pressure is increased 20 mm.?

4. Given 88 c. c. of hydrogen gas at 21°C . Find its volume at 42°C .

5. A gas measures 150 c. c. at a temperature of -10°C . Find its volume at 10°C . (The student may be interested in trying to

solve this problem by using Centigrade temperatures. Is the result reasonable?)

6. A gas has a volume of 180 c. c. when the temperature is 45°C . What temperature is needed to reduce the volume of the gas to 120 c. c.?

7. Reduce to standard conditions: 1200 c. c. of gas at 30°C . and 800 mm. pressure.

8. Reduce to standard conditions: 1500 c. c. of gas at -20°C . and 700 mm. pressure.

9. Reduce to standard conditions: 800 c. c. of gas at -30°C . and 780 mm.

10. Given 100 c. c. of gas measured at 0°C . and 380 mm. pressure. What will be the volume at 273°C . and 760 mm. pressure?

11. A gas measures 250 c. c. when the temperature is 27°C . and the pressure is 775 mm. If the temperature is increased to 36°C ., what pressure must be used to keep the gas at the same volume?

12. A gas collected when the temperature is 18°C . and the pressure is 810 mm. measures 450 c. c. Find its volume the next day when the thermometer reads 24°C . and the barometer reads 745 mm.

13. One liter of oxygen weighs 1.43 gm. at S. T. P. Find the weight of one liter of oxygen when the temperature is 21°C . and the pressure is 720 mm.

14. 225 c. c. of gas weigh 4.5 gm. when the temperature is 15°C . and the pressure is 78 cm. of mercury. Find the weight of 22.4 liters of this gas at S. T. P.

15. Reduce to standard conditions: 500 c. c. of oxygen collected over water when the temperature is 18°C . and the pressure is 765.3 mm.

16. Reduce to standard conditions: 600 c. c. of gas collected over mercury. Temperature, -15°C .; pressure, 733 mm.; inside level 33 mm. lower than outside level.

17 Reduce to standard conditions: 950 c. c. of gas collected over water. Temperature, 27°C .; barometer, 754.5 mm.; outside level is 136 mm. lower than inside level.

18. Given the following conditions: A gas collected over water measures 1500 c. c. at a temperature of 24°C . and a pressure of 776 mm.; the outside level is 54.4 mm. higher than the inside level. Find the volume of the dry gas at standard conditions.

CHAPTER VIII

WATER—COMPOSITION AND PROPERTIES

71. Occurrence. We have already studied two common elements, hydrogen and oxygen. Let us next turn our attention to a compound of these two elements, water. Water is one of the most useful compounds, and it is also one of the most abundant. Nearly three-fourths of the earth's surface is covered with water. In the air we find it present as a vapor. Our foods are rather more than half water. For example, bread is a little less and meat a little more than 50% water by weight. About 75% of most vegetables is water, and milk contains about 88%.

72. Physical Properties. Pure water is odorless and tasteless. Any odor or taste in drinking water is due to impurities dissolved in the water, either mineral matter, carbon dioxid, or other gases. In small quantities water is colorless, but deeper layers have a blue tint.

At ordinary temperatures water is a liquid, but it changes into ice at 0° C., or 32° F. In solidifying, water expands slightly; therefore the ice that is formed is lighter than water and floats with about $9/10$ of its volume submerged. In other words, ice is approximately 0.9 as dense as water. One cu. ft. of ice weighs a trifle more than 57 lb.

Water under a pressure of 760 mm. of mercury (one atmosphere) boils at 100° C. or 212° F. The steam that is formed occupies about 1600 times as much space as the water originally occupied. It is the expansive force which water exerts as it evaporates that gives steam its ability to run engines. As the pressure of the air upon the water surface is decreased, water boils at a lower temperature. If the pres-

sure is reduced to about 47 mm. of mercury, water boils at 37° C., or at body temperature. The tendency of liquids to boil at lower temperatures when the pressure is reduced is common to all liquids. In the industries "vacuum pans" are extensively used to facilitate rapid drying at low temperatures.

73. Water Used as a Standard. Since water is so abundant and so easy to obtain in a fairly pure condition, it is used as a standard in *specific weight* and *specific heat* determinations. When we use the word "specific," we imply a ratio. The specific weight of a substance is that number which tells how many times as heavy that substance is as the same volume of water.
$$\text{Specific weight} = \frac{\text{density of substance}}{\text{density of water}}.$$

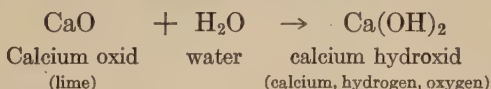
Water has its greatest density at a temperature of 4° C. At this temperature 1 c. c. of water weighs 1 gram. Air or hydrogen may be used as the standard for gas densities.

Water heats slowly and cools slowly. Therefore large bodies of water exert much influence in moderating the climate of a place. Our definition of the calorie tells us that it takes 1 calorie to raise the temperature of 1 gram of water 1° C. The number of calories needed to raise the temperature of 1 gm. of any substance 1° C. compared to the number of calories needed to raise the temperature of 1 gm. of water 1° C. is the *specific heat* of that substance.

74. Chemical Properties. 1. *Stability.* If a compound is quite easily decomposed into its elements, it is said to be *unstable*. We know that Priestley split mercuric oxid up into its elements by focussing the heat from the sun by means of a burning glass. Since water is an oxid of hydrogen, we might expect it to behave in a similar manner. But unfortunately we can not assume in chemistry that all oxids will act alike under similar conditions. In fact water is so *stable* that less than 2% is decomposed at the very high temperature of 2000° C.

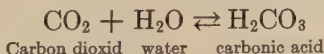
2. *Action with Metals.* In the preparation of hydrogen we found that certain active metals interact readily with water to liberate hydrogen. Sodium, potassium, calcium, and a few other metals decompose water at the ordinary temperature. Magnesium decomposes hot water, and aluminum, zinc, and iron when heated red hot interact with water.

3. *Action with Metallic Oxids.* A large majority of the oxids of metals are insoluble in water. Some of the more active metals form oxids, however, which interact with water. Every student has probably observed a mason slaking lime. The lime unites with the water chemically with the evolution of much heat, enough under certain conditions to raise the temperature of wood to its kindling point. The compound formed is *calcium hydroxid*.



When water unites with the oxids of metals, it forms a class of compounds known as *hydroxids*. They contain a metal, hydrogen, and oxygen. To the chemist these compounds are known as *bases*. The soluble active bases are called *alkalis*.

4. *Action with Non-metallic Oxids.* The oxids of such non-metals as sulfur, carbon, nitrogen, and phosphorus combine with water readily. The products formed are known as *acids*, and their properties are quite the opposite to those of the bases. The following equation shows what happens when carbon dioxide is added to water:



The reaction is reversible, and carbon dioxide passes off as a gas when carbonic acid is heated.

5. *Hydrates.* Water unites with many compounds as they crystallize from water solution, forming *hydrates*. Several

molecules of water may thus combine with one molecule of a compound. When such a *hydrated* compound is heated, it generally loses water. The process is one of *dehydration* and the residue is said to be *anhydrous* (without water).

6. *Water Brings about Chemical Changes.* When water is added to baking powder a gas is evolved and chemical action begins immediately. In many cases no action between chemicals is apparent in the *dry* state. As soon as water is added, the action begins. The water appears to act as a general catalyst. In fact some chemists maintain that a trace of moisture is a requisite for chemical action. Experiments have shown that perfectly dry hydrogen and oxygen do not explode when mixed and ignited. We all know that a gasoline

engine runs better when the air contains considerable moisture. The reason for this action of water will be more fully discussed in the chapter on ionization.

7. *Hydrolysis.* Some compounds are decomposed when they are added to water. *Hydrolysis*, or *the decomposition of a compound by water*, will be more fully discussed in a later chapter.

75. Composition of Water by Volume. Under the preparation of hydrogen and oxygen, we learned that water may be decomposed by means of the electric current. If we



FIG. 52.—Eudiometer tube for measuring gases.

collect both gases by the use of an apparatus like that shown in Fig. 9, we shall find that *2 volumes of hydrogen* are liberated to *1 volume of oxygen*. The analysis of

water always yields these elements in the same proportion by volume.

Further proof that water is composed of hydrogen and oxygen in the proportion of two to one may be had by recombining these elements to form water. Fig. 52*a* shows a eudiometer tube arranged for collecting gases by mercury displacement.

Suppose we introduce 20 c. c. of hydrogen and 10 c. c. of oxygen into the tube as shown in Fig. 52*b*, and pass an electric spark between the wires *w* and *w'*. The mixture explodes and water vapor is formed. As the vapor condenses, the mercury rises in the tube. No hydrogen or oxygen is left uncombined. If we start with 20 c. c. of hydrogen and 20 c. c. of oxygen, the explosion takes place as before, but 10 c. c. of oxygen are left uncombined. If we use 30 c. c. of hydrogen and 10 c. c. of oxygen, then we have 10 c. c. of hydrogen remaining uncombined. All attempts to make hydrogen and oxygen combine directly in any other ratio by volume than 2 to 1 result in failure.

76. Composition of Water by Weight. An American chemist, Edward William Morley, is well known for his very accurate work in determining the composition of water by weight. He weighed the hydrogen and the oxygen, and then the water that was produced by their union. As a result of his experiments, he found that one part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form 8.94 parts by weight of water. To weigh gases in a vacuum at standard conditions of temperature and pressure involves such refinement of apparatus and such careful manipulation that some indirect method of finding the composition of water by weight is more often used. The following method was devised by Dumas, a French chemist.

A weighed quantity of copper oxid is placed in a hard glass tube, as shown in Fig. 53. *Dry* hydrogen is then passed over the *heated* oxid, reducing the copper oxid to metallic copper, and uniting with the oxygen to form water. The

water thus formed is absorbed in a previously weighed tube containing granular calcium chlorid. The copper oxid tube shows a loss of weight due to the abstraction of oxygen. The calcium chlorid tube shows an increase in weight due to the absorption of water. Suppose we start with 23.8 gm. of copper oxid. After heating it weighs 15.86 gm. The loss of weight, 7.94 gm., is the weight of the oxygen used to form water. The calcium chlorid tube weighed 80 gm. before the experiment and 88.94 gm. after its completion. The gain in weight, 8.94 gm., is the weight of the water formed: $7.94 \div 8.94 = 88.81$, the per cent of oxygen. One gram, the weight

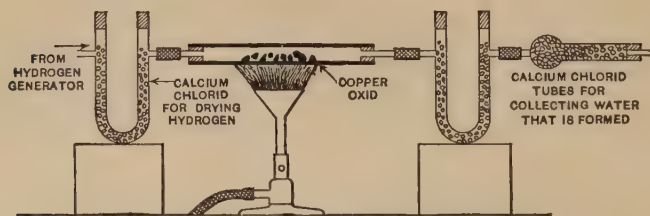


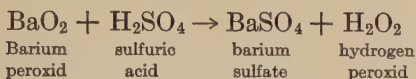
FIG. 53.—Composition of water by weight.

of hydrogen which must have combined with the oxygen, divided by 8.94 equals 11.19% hydrogen. Therefore water is made up of 88.81% of oxygen by weight, and 11.19% of hydrogen. It is *approximately* correct to say that 1 gm. of hydrogen combines with 8 gm. of oxygen to form 9 gm. of water.

77. Hydrogen Peroxid. Although 2 hydrogen atoms unite directly with 1 atom of oxygen, it is possible by the use of indirect methods to form a compound in which 2 atoms of oxygen are combined with 2 atoms of hydrogen. This compound, which is called *hydrogen peroxid*, has the formula H_2O_2 .

1. *Preparation.* Hydrogen peroxid is prepared by treating barium peroxid with a cold dilute solution of sulfuric acid.

The reaction is one of double decomposition, or metathesis, as shown by the following equation:



2. *Properties.* Pure hydrogen peroxid is a syrupy liquid, about $1\frac{1}{2}$ times as heavy as water. The pure liquid is unstable and may explode violently. Therefore hydrogen peroxid is put on the market in a dilute aqueous solution containing about 3% of the peroxid. Such a dilute solution keeps fairly well, unless exposed to light. One bottle of such a solution yields by decomposition 10 bottles of oxygen, hence the expression "10 V." so frequently seen on the label.

The decomposition of hydrogen peroxid yields nothing but oxygen and water.



When an element is just being liberated from a compound it is *especially active chemically*. It is then said to be in the *nascent state*. A compound which is quite unstable and which sets free nascent oxygen as it breaks up is a good oxidizing agent.

3. *Uses.* Oxidizing agents destroy the color of many organic compounds; they also kill bacteria. Therefore hydrogen peroxid is used to bleach wool, silk, hair, ivory, and feathers, since animal products are apt to be injured by chlorin or other bleaching agents. Hydrogen peroxid also finds use in cleansing wounds, although its desirability for this purpose appears to have been over-estimated. Some physicians claim that hydrogen peroxid irritates the wound causing it to heal more slowly. As a result they recommend the use of iodine for sterilizing surface wounds.

78. Law of Multiple Proportions. Quite often we find that two elements may unite to form more than one com-

pound; thus hydrogen and oxygen unite to form water (H_2O) and hydrogen peroxid (H_2O_2). The law of definite proportions holds true for each of these compounds, since the water is made up of approximately 8 parts by weight of oxygen to 1 part by weight of hydrogen, and the hydrogen peroxid is made up of about 16 parts by weight of oxygen to 1 part of hydrogen.

John Dalton, the same man who formulated the law of definite proportions, studied several series of compounds and stated the law of *multiple proportions*: *Given two elements which unite to form a series of compounds; if we consider a fixed weight of one element, which we may call "A," then the weights of the other element, "B," will be in the ratio of small whole numbers.* Hydrogen peroxid has one more atom of oxygen in its molecule than water has, hence the weight of the oxygen is just double, for all atoms of oxygen have the same weight. In the foregoing example, the weight of the hydrogen, or element "A", may be considered as 1; then the relative weights of oxygen, or element "B," are 8 and 16 respectively. Their simplest ratio is 1 to 2, small whole numbers. Since 16 is a multiple of 8, the law is known as the law of *multiple proportions*.

SUMMARY

Water is one of the most abundant compounds.

Water is colorless, odorless, and tasteless. It freezes at 0°C . and boils at 100°C . One cubic centimeter of water at 4°C . weighs 1 gram.

Chemically water interacts with several metals. It unites with the oxids of metals to form *bases*. It unites with the oxids of non-metals to form *acids*. It unites with many compounds as they crystallize, forming *hydrates*.

By analysis it has been shown that water is made up of two volumes of hydrogen to one volume of oxygen. By uniting these elements in the same ratio water is formed.

Water contains 1 part by weight of hydrogen to 7.94 parts by weight of oxygen.

Hydrogen peroxid is used as an oxidizing agent; as a disinfectant; and as a bleaching agent.

When two elements unite to form a series of compounds, if we consider a fixed weight of one element, "A," then the weights of the other element, "B," will be in the ratio of small whole numbers.

QUESTIONS

1. How would natural conditions be affected if water contracted upon solidification?

2. Explain the principle of the "hot water bottle" as used in sick rooms.

3. How does water moderate the climate of such places as Honolulu? Does it produce a similar effect on the climate of Boston?

4. Why is water such an important compound from the standpoint of chemistry?

5. Why is hydrogen peroxid generally kept in brown-colored bottles?

6. How could you determine the per cent of water in milk?

7. Would water be useful in putting out a fire if the temperature were 2500° C.?

PROBLEMS

1. Suppose we mix 45 c. c. of hydrogen with 20 c. c. of oxygen and explode the mixture. What gas remains and what is its volume?

2. What gas is left after a mixture of 75 c. c. of oxygen and 80 c. c. of hydrogen are ignited? What is its volume?

3. How many grams of water would be formed by burning 23.82 gm. of oxygen in the presence of 8 gm. of hydrogen? How many grams of hydrogen would be left uncombined? Is it correct to speak of burning oxygen in this case?

4. Air is 21% oxygen; 25 liters of air are mixed with 4 liters of hydrogen and the mixture is ignited. How many c. c. of gas are left?

5. Given 600 c. c. of hydrogen measured at 24° C. and 80 cm. pressure and 300 c. c. of oxygen measured at — 50° C. and 780 mm. pressure. What gas is left after the mixture is exploded and what is its volume at S. T. P.?

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CHAPTER IX

SOLUTION—CRYSTALLIZATION

79. Solution. One of the most important properties of water is its ability to dissolve certain substances. If we add a little sugar to water, the sugar gradually disappears. It goes into solution in the water, but it does *not melt*, as some incorrectly state. The liquid that is used to bring about solution is called the *solvent*. The substance that goes into solution is called the *solute*. Let us add a small crystal of potassium permanganate to a liter of more of water, and stir the liquid until the crystal has all dissolved. Every drop of this solution will have a reddish-purple tint, thus showing that in solution the particles are finely divided. If we put a drop of the solution under a compound microscope, we can not see the small particles of the solute.

If we stir our coffee until the sugar is all dissolved, a spoonful from the top will be just as sweet as one taken from the middle or from the bottom of the cup. When a cold solution stands, the solute does not separate from the solvent.

A solution has the following characteristics: 1. It is homogeneous, having the same nature throughout; 2. The particles of the solute are very finely divided and they can not be removed by passing the solution through a filter; 3. The solute does not separate from the solvent upon standing unless the temperature changes or some of the solvent evaporates. Material suspended in a liquid tends to separate upon standing. Thus we see that *a solution is really a uniform mixture consisting of a solvent and the solute.*

The question whether solution is a physical or a chemical change is one upon which chemists are still in doubt. It seems reasonably certain that chemical action occurs in

dissolving some compounds. In other cases the action appears to be physical. When water is the solvent, the solute often unites with it to form hydrates. In such a case this part of the action is doubtless chemical, but if the hydrate then dissolves in the excess water that is present, the action is probably physical. It is incorrect to say that metals dissolve in acids. They interact with the acid to form a new compound, which may then dissolve in the excess water which was present in the acid.

80. Saturation. If a solution were a true compound we could dissolve only a definite amount of solute in a given quantity of solvent. We know, however, that we can dissolve a few crystals of salt in 100 c. c. of water, or that we can dissolve several grams. When only a few crystals are added we form a *dilute* solution. As we continue to add more salt, the solution becomes more *concentrated*. If we continue to add salt, we finally reach a point where no more salt will dissolve unless we raise the temperature. When a solvent under these conditions holds all the solute it can, *the solution is said to be saturated with salt at that temperature.*

When we speak of a *dilute* solution we refer to a solution containing a relatively small proportion of the solute; a *concentrated* solution contains a relatively large proportion of the solute.

The ratio between the weight of the solute and the weight of the solvent required to saturate a solution is known as the solubility of the solute at that temperature. If we refer to Table 6, page 555, we find that the solubility of potassium nitrate is 26.0 gm. per 100 gm. of water at a temperature of 20° C.

We speak of a substance as being *insoluble*, if the total quantity that can be dissolved is very small. Strictly speaking, nearly all substances dissolve in water to a *slight* extent. Students are generally surprised to learn that chemists test the solubility of different kinds of glass.

81. Solution of Solids, Liquids, and Gases. The solute may be a solid, a liquid, or a gas. Water is one of the best solvents known, as many different substances are more or less soluble in water. Other well-known solvents include alcohol, gasoline, turpentine, ether, and carbon tetrachlorid. An alcoholic solution of a non-volatile substance is called a *tincture*. For example, tincture of iodine is a 7% solution of iodine in alcohol. A water solution of potassium iodide dissolves iodine. Such a solution may be used instead of the tincture.

When two liquids are mutually soluble, they are said to be *miscible*. Alcohol and water are miscible in all proportions. Oil and water are *immiscible*. When an oily liquid is vigorously shaken with water the finely divided particles of oil remain *temporarily* suspended in the water forming an *emulsion*. Milk is a good example of an emulsion as the fat globules remain suspended for some time before the cream separates. Several substances may be used to make emulsions more permanent. Gums have this property. The cleansing action of soap is largely due to its ability to form emulsions with grease. In making mayonnaise dressing egg yolks are added to make the emulsion of olive oil permanent.

Most gases are to some extent soluble in water; in some cases several volumes dissolve in one volume of water.

82. Effect of Temperature on Solubility. The solubility of a solid depends upon the nature of the solid itself, upon the solvent used, and also upon the temperature. See Fig. 54. In general *an increase in temperature increases the solubility of a solid*. For example, 100 grams of water at 30° C. dissolve only 44 grams of potassium nitrate, while at 70° C. the same weight of water dissolves 140 grams of potassium nitrate. By reference to the solubility curves on page 97, the student will get a good idea of the effect of temperature and the nature of the solid on solubility. Table 6 shows that a few substances, calcium hydroxide for example, are less soluble in hot water than in cold.

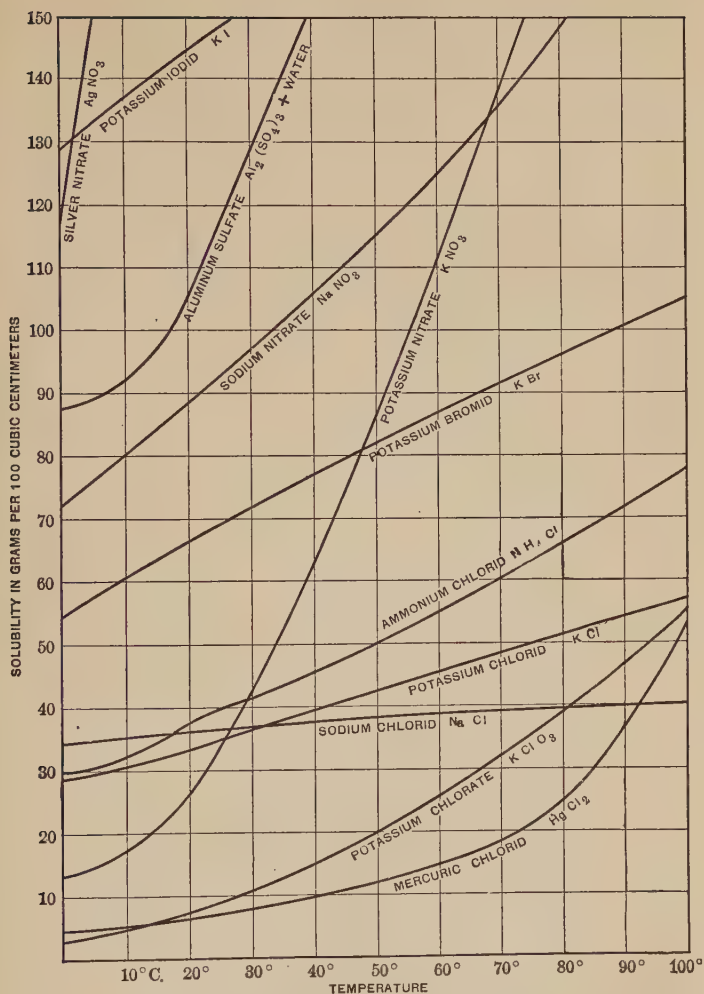


FIG. 54.—Curves showing the effect of temperature on solubility.

As in the case of solids, the solubility of liquids increases as the temperature rises, until the boiling point of one of the liquids is reached.

Gases, however, are less soluble at higher temperatures. Heating a solution of a gas causes some of the gas to escape. The bubbles that arise when water is first heated are air bubbles. Their evolution is due to a decrease of solubility with increased temperature.

83. Effect of Pressure on the Solubility of Gases. When a gas is forced into a solvent under increased pressure its solubility is much increased. In fact the *solubility of a gas is directly proportional to the pressure at which the gas is supplied*. This statement is known as Henry's law. It is put to practical use in bottling carbonated waters and in charging soda fountains, where carbon dioxid is forced into the solvent under a pressure of from 5 to 10 atmospheres. When soda water is drawn from the fountain the carbon dioxid gas escapes with *effervescence*.

84. Speed of Solution. We may hasten the speed at which a solid dissolves in three ways: (1) *by stirring*. Agitating the mixture brings fresh portions of the solvent in contact with the solute; (2) *by powdering the solid*. Since solution occurs only at the surface of a solid, powdering the solute increases the amount of surface that comes in contact with the solvent; (3) *by heating*, since an increase in temperature usually increases the solubility.

85. Freezing Point and Boiling Point of Solutions. A solution always freezes at a temperature *lower* than the freezing point of the pure solvent. When an unsaturated solution *begins* to freeze, the pure solvent solidifies and the solute it contained forms with the rest of the solvent a more concentrated solution. Thus the freezing point is *lowered* still more until the solution finally becomes saturated. A saturated solution has a constant freezing point. For example, a saturated solution of sodium chlorid freezes at -22°C .

The boiling point of a solution also differs from that of the pure solvent. As the solution of a non-volatile solid boils the solvent disappears by evaporation and the solution becomes more concentrated until it is finally saturated. In the meantime the boiling point gradually *rises* as the solution becomes more concentrated.

If the solute is more volatile than the solvent, the solution generally boils at a *lower* temperature than the pure solvent, and at the same time it becomes more dilute. When a solution of ammonia is boiled the ammonia escapes as a gas and the boiling point of the solution rises gradually.

86. Crystallization. If we cool a hot saturated solution, some of the solute usually separates from the solution in the form of crystals. The shape of the crystal depends upon the nature of the substance, but it is generally that of some regular geometric figure. Salt crystals are cubes; alum and diamond crystals are octahedral. Since the shape of the crystal is peculiar to the substance, it is quite often possible to identify a substance by the form of its crystals. See Fig. 55. Crystals also separate from a saturated solution as the solvent evaporates. Many substances assume a crystalline form when they freeze, or change from a liquid to a solid state. Iron, sugar, sulfur, and water are examples. Some substances, glue and gelatin as examples, do not crystallize as they solidify.

87. Importance of Crystallization. We know that some substances may be identified by the shape of their crystals, but crystallization is of much greater use in purifying chemicals. Suppose we have two salts dissolved in water. Since practically no two salts have the same solubility, the *less* soluble salt will crystallize first when the solution is cooled or evaporated. The other salt remains in the "mother liquor." By further evaporation other crystals are obtained. The first crop of crystals is the purest. The process is known as *fractional crystallization*. The crystals may be still further

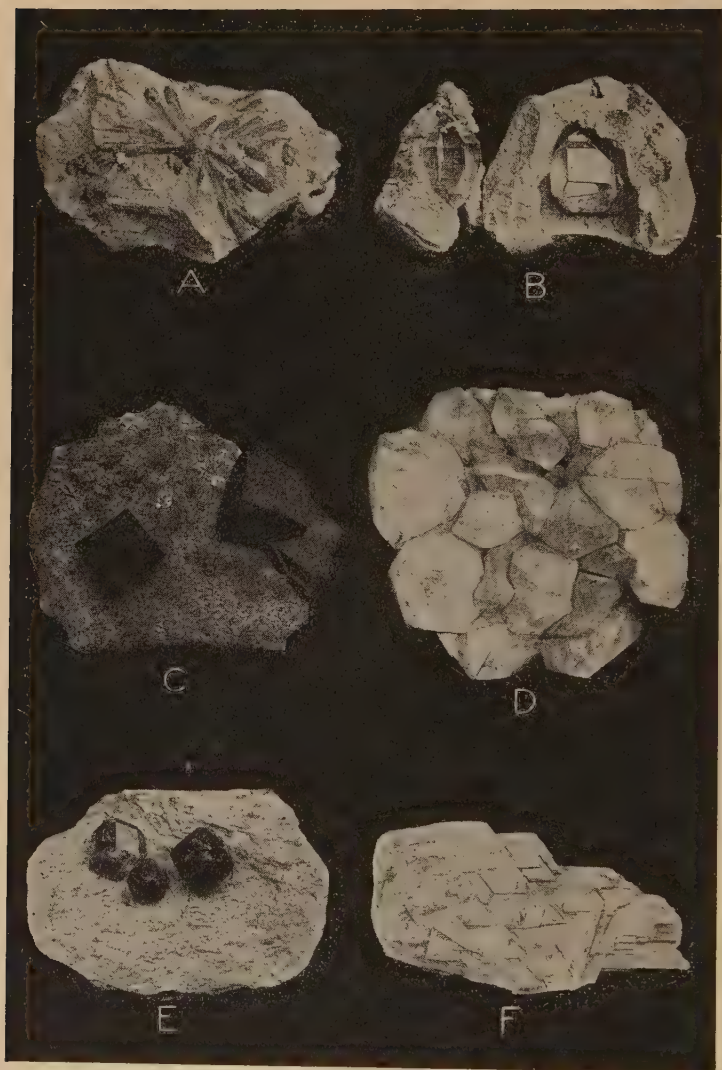


FIG. 55.—Plate of crystals. *a.* Rubellite. *b.* Quartz crystal in matrix. *c.* Galena. *d.* Quartz crystals. *e.* Garnets on rock. *f.* Gypsum.

purified by dissolving them in pure water and *recrystallizing*.

If the solution is stirred while crystallization is taking place, finer crystals are formed. Small crystals thus rapidly produced are generally purer than large crystals formed more slowly, since the latter are more apt to have incorporated in them some of the mother liquor. If crystals that contain water thus mechanically held are heated they *decrepitate*. Steam is formed within the crystal and its expansion causes the crystal to burst open with a snapping sound.

If one looks over a stock of chemicals, he will find many different terms used to indicate the purity of the different chemicals. Some low-grade material is marked "commercial," or "technical." Purer chemicals may be marked "pure," "recrystallized," "U. S. P.," "highest purity," "crystallized from alcohol," and "C. P.," or "chemically pure." Unfortunately, *absolute* purity is impossible. Many manufacturers of chemicals now send out "Analyzed Chemicals," in which the analysis is printed on the label. Then the chemist can tell just what impurity is present and in what quantity.

88. Supersaturated Solutions. Sometimes a solution saturated at a high temperature may be cooled without precipitating any of the dissolved solid in the form of crystals. For example, a solution saturated with ordinary "hypo" at a temperature of 60° or 70° C. may be cooled to room temperature without depositing any crystals. Such a solution is said to be *supersaturated*. It contains more of the solute than a saturated solution can hold under normal conditions. When a fragment of "hypo" is added to such a solution, crystals begin to form immediately. The crystallization continues until all the excess solute has separated, leaving a solution saturated at the lower temperature. Stirring a supersaturated solution or scraping the inside of the containing vessel usually starts the crystallization. Some substances

readily form supersaturated solutions; others show this tendency to a very slight degree only.

89. Water of Crystallization. Many salts combine with one or more molecules of water when they separate from solution in the form of crystals. For example, crystallized copper sulfate has the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, showing that each copper sulfate molecule combines with five molecules of water as it crystallizes. Such a compound is called a *hydrate*, and the crystal is said to contain *water of crystallization*. Water mechanically held by a crystal either by adhering to it or by being inclosed within the crystal must not be confused with water of crystallization. That water of crystallization is chemically combined with the substance is shown by the fact that hydrates follow the law of definite proportions.

When crystallized copper sulfate is heated it loses water, its glassy luster disappears, its color changes from blue to white, and a powder is formed. Such removal of water from a crystal is called *dehydration* and the substance left is said to be *anhydrous*. The formula for anhydrous copper sulfate is CuSO_4 . If water is added to anhydrous copper sulfate a blue solution is formed. From this solution *hydrated* copper sulfate crystals may again be obtained by evaporating part of the solvent.

Sodium carbonate crystallizes with 10 molecules of water, nearly 63% by weight; sodium sulfate has 10 molecules of water of crystallization, or nearly 60%. The student must not get the idea that all crystals are hydrated. For example, sodium chlorid, potassium chlorid, potassium nitrate, and potassium chlorate have no water of crystallization.

90. Efflorescence. Some crystals hold their water of crystallization so loosely that they lose a part or all of their water without being heated. A crystal that loses its water of crystallization when exposed to the air at ordinary temperature is said to be *efflorescent*. If we put on a scale pan a few freshly prepared crystals of sodium sulfate or sodium car-

bonate, and put enough shot on the other pan to counterpoise them, the crystals show a loss of weight after a few minutes' exposure. Water is given off and the crystals lose their luster, crumbling to a powder. *Efflorescence* occurs more readily in a very dry atmosphere than during damp rainy weather.

91. Deliquescence. Crystals of zinc chlorid, magnesium chlorid, and calcium chlorid take moisture from the air on exposure, and become wet, or even dissolve in the water thus absorbed. This property is known as *deliquescence*. It is much more pronounced in damp weather.

Crystals like common table salt which attract moisture so that a slight film forms on their surface are called *hygroscopic*. Common table salt usually contains as an impurity a slight trace of some deliquescent substance. Hence it becomes wet in damp weather and "packs." Pure sodium chlorid is not deliquescent.

Deliquescent substances are used extensively for drying other substances. In the experiments on reduction and on determining the composition of water, the hydrogen was dried by passing it through a tube filled with calcium chlorid, a deliquescent substance. The water formed in the latter experiment was absorbed by the same compound. Fig. 56 shows a desiccator used for drying compounds in the laboratory. The lower compartment is filled with deliquescent crystals.

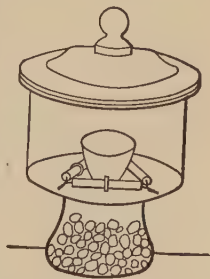


FIG. 56.—Desiccator.

SUMMARY

A solution is a homogeneous mixture consisting of a *solvent* and the *solute*.

Liquids that are mutually soluble in each other are said to be *miscible*.

The *concentration* of a solution is the weight of solute in a given quantity of solvent. In a *dilute* solution the concentration is small; in a *concentrated* solution it is large; in a *saturated* solution the concentration is at its maximum.

An increase of temperature *increases* the solubility of solids; it *decreases* the solubility of gases. An increased pressure increases the solubility of gases in liquids.

The speed of solution may be hastened: (1) *by stirring*; (2) *by raising the temperature*; (3) *by powdering the substance*.

Cooling a saturated solution causes a part of the solute to separate as crystals. Evaporation produces the same effect.

Water interacts with certain salts when they crystallize, thus forming *hydrates*. Hydrates lose their water of crystallization when they are heated; some hydrates lose water on exposure to the air at ordinary temperature. They are said to be *efflorescent*.

Some substances absorb water from the air and dissolve in the water thus absorbed. This property is known as *deliquescence*.

QUESTIONS

✓1. How would you proceed to prepare a saturated solution of a salt?

✓2. Given a solution of sodium sulfate. How could you tell whether it is unsaturated, saturated, or supersaturated?

3. If you were given a solution containing sodium chlorid and potassium nitrate, how would you separate the two salts? Would the method be suitable for use at a temperature of 25° to 30° C.? Refer to the curves of solubility and explain.

✓4. When emulsions are used as medicines, why should the bottle be thoroughly shaken before using?

✓5. Why do soda fountains sometimes burst or explode?

✓6. Account for the rapid effervescence when a glass of "soda water" is drawn. Why do bubbles of gas continue to rise more slowly as the liquid stands for a time?

7. Why are crystals of sugar often found in preserves that have stood a long time?

8. Why do vegetables cook faster in a strong salt solution than in fresh water?

✓9. How does a solution differ from a chemical compound?

✓10. Why should bottles of calcium chlorid be kept tightly stoppered?

11. Would you prefer to buy crystals of washing soda (sodium

carbonate) that had been kept in stoppered or in open boxes, if the price per pound were the same? Explain.

12. What advantage is gained by putting small unstoppered bottles of calcium chlorid in the cases of clocks, electrical machines, and accurate balances?

✓ 13. How would you use anhydrous copper sulfate as a test for water?

14. How does leaving the iodine bottle unstoppered affect the concentration of the tincture? What danger might result from such practice?

✓ 15. The expression "concentrate by evaporation" is often used by chemists. What is its meaning?

*End
Thursday.*

CHAPTER X

PURIFICATION OF WATER—HARDNESS

92. Impurities in Water. Since water is such a good solvent, and no substance is absolutely insoluble, it is practically impossible to obtain pure water. The impurities present in water may be held: (1) in *suspension*; (2) in *solution*. Because of its buoyant effect water holds material in suspension. When water is in motion, upward currents are more or less prevalent. Thus it is possible for running water to carry more material in suspension. The amount of material water can carry depends upon the size of the particles and upon their density; it also increases as the velocity of the water is increased. When water stands quietly all the matter it held in suspension drops as sediment unless the matter had a density less than that of the water itself.

Rain water has very little matter in solution. It is *soft* water. Ground water contains considerable mineral matter in solution, since water is such a good general solvent. Water that contains more than 50 parts of mineral matter dissolved in 1,000,000 parts of water is classed as *hard* water. Very hard water has over 100 parts per million. Some especially hard waters have 400 parts of mineral matter per 1,000,000.

93. Kinds of Impurities. Impurities in water are classed as: (1) *organic*; (2) *inorganic, or mineral*. Organic matter consists of bacteria, sewage, and other forms of animal and vegetable matter in various stages of decomposition or decay. As plants and animals decay, ammonia is formed. This ammonia is slowly oxidized first to nitrites and then to nitrates. The presence of more than a trace of ammonia, nitrites, or nitrates in drinking water indicates sewage con-

tamination, or that the water is unwholesome. Much organic matter in water renders it unfit for drinking purposes, since such matter, though often harmless in itself, forms a breeding ground for all kinds of bacteria.

Either harmless or disease-producing bacteria may be present in drinking water. Epidemics of typhoid fever, dysentery, and cholera have often been traced to contaminated water supply. Typhoid fever has been nearly stamped out in cities where proper methods of purifying the water supply have been installed. During the Spanish-American War in 1898 typhoid fever caused the death of more soldiers than did the Spanish bullets. But methods of improving the sanitary conditions of drinking water have improved so much that very few men died from typhoid during the World War. In the summer of 1898 the death rate from typhoid was 897 per 100,000 men. During the summer of 1918 it was only 3.3 per 100,000 men.

The nature of mineral matter in solution in water depends upon the composition of the soil and rock through which the water flows. Compounds of calcium, magnesium, sulfur, and iron are among the most common substances found in hard water. Since calcium compounds are found in the bones and teeth, their presence in water that is to be used for drinking purposes is thought by some doctors to be desirable. Other doctors claim that mineral matter from hard water is not assimilated by the body at all.

94. Methods of Purification. Matter in *suspension* may be nearly all removed from water by three common mechanical processes: (1) by *sedimentation*; (2) by *sedimentation with coagulum*; (3) by *filtration*.

Organic matter is generally to a greater or lesser degree destroyed by the use of one or more of the following processes: (1) *aëration*; (2) *light*; (3) *ultra-violet rays*; (4) *boiling*; (5) *cold*; (6) *the use of chemicals*.

Volatile matter is driven off when water is boiled, but

non-volatile matter in *solution* can be removed only by *distillation*.

95. The City Problem. In the country a farmer can get a supply of pure water by drilling a well deep enough to get water that has not been contaminated. Of course his well must be walled so that surface water can not flow into



FIG. 57.—Filtration beds showing connection with water mains.

it. If it is down in the valley, it must be protected against drainage from the stables or barns.

But as a city increases in size, the problem of securing an adequate supply of wholesome water becomes increasingly difficult and costly. Large areas must often be bought by the city, and the water in the lakes or streams within such area must be kept as free from organic refuse as possible. Of the methods of purifying water named above filtration is most often used, either alone or in combination with other methods. If the water is roily it first goes to settling tanks or reservoirs.

96. Sedimentation. When water that contains material in suspension flows into the settling tanks, it soon loses nearly all such matter on account of the influence of gravity. This method of purification or sedimentation with coagulum is often used preliminary to filtration.

97. Sedimentation with Coagulum. Aluminum hydroxid

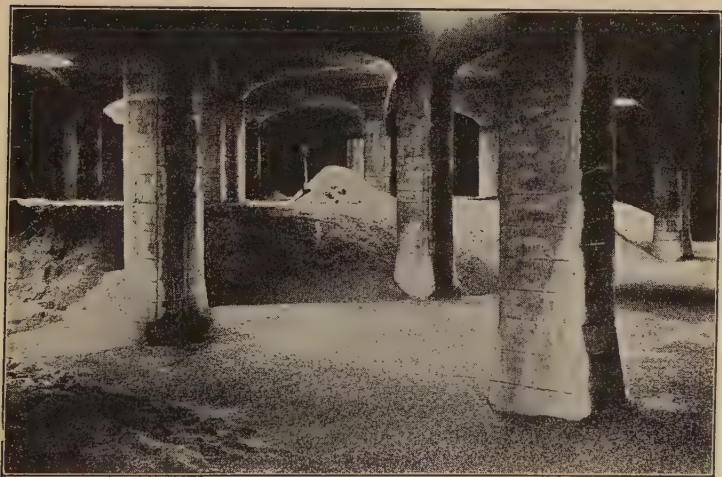


FIG. 58.—A portion of the same filtration beds filled with sand ready for filtration.

is an insoluble compound, bulky and gelatinous in its nature when mixed with water. It is formed when aluminum sulfate is added to water that contains certain mineral matter. Sometimes if the water is quite soft a certain amount of slaked lime is added to the water with the aluminum sulfate. The slaked lime interacts chemically with the aluminum sulfate to form aluminum hydroxid. As this bulky precipitate settles, nearly all the materials in suspension, including a large per cent of the bacteria present, are enmeshed and carried down with it. The bulky precipitate is commonly called *coagulum*. The hardness of the

water may be slightly increased by the addition of the slaked lime.

98. Filtration. Water from wells and springs is purified by *natural soil filtration*. As the water trickles through the soil the impurities in suspension are strained out. Destruction of the bacteria and organic matter occurs by oxidation. The efficiency of this method of purification depends upon the nature of the soil and the distance the water travels through uncontaminated soil. A sandy or gravelly soil

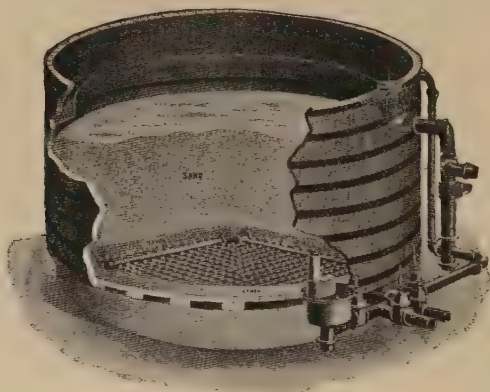


FIG. 59.—Gravity type of mechanical filter.

is best. If the well is in a valley and near-by houses and stables are situated on higher ground, the soil through which the water flows may become contaminated with pathogenic bacteria. Filtration through such a soil is a menace.

Slow Sand Filters. City water is often filtered through layers of sand and gravel acres in extent and several feet thick. Layers of charcoal may be used between the sand and gravel to remove coloring matter and gases having disagreeable odors. At the bottom the filtered water collects in tile drains which transmit it to the city mains. See Fig. 57. A gelatinous layer soon collects on the top thus

aiding the purification, partially because of more perfect filtration and partially because microorganisms that destroy bacteria collect in this layer. As the rate of filtration becomes more and more retarded, it is necessary to scrape off this surface layer occasionally. These filtration plants are expensive to install, since they should be covered to prevent freezing. See Fig. 58. In the presence of sunlight certain plants known as algæ grow readily in water reservoirs. They are sometimes called "pond-scum." Some varieties secrete an oily substance that gives to water a disagreeable fishy, or pig-pen, odor.

Mechanical Filters. Mechanical filters are rapid sand filters that are generally used with coagulation systems. The water is run into large tanks and treated with the chemicals as in the coagulum method described above. The partially clarified water is then strained rapidly through the sand and gravel layers in the mechanical filter. Fig. 59 shows a mechanical filter of the gravity type.

In Fig. 60 a pressure filter is shown. When mechanical filters need to be cleaned water is forced through them in the reverse direction, the impurities being carried into the sewer with the wash water. The re-

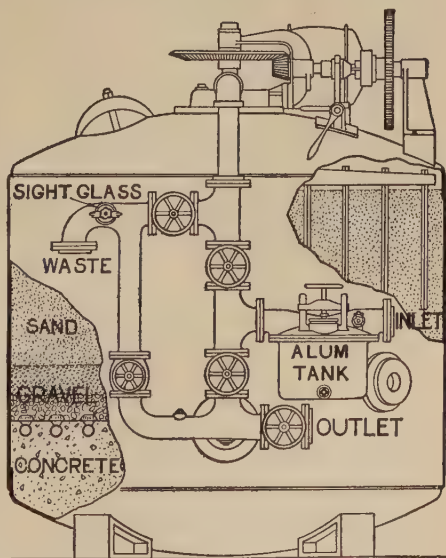


FIG. 60.—Mechanical filter of the pressure type.

volving rakes shown in the figure aid the cleansing process by breaking up the bed of filtering material.

99. Household Filters. Many persons have the idea that a bag of charcoal tied over the faucet or pump-spout will filter out all impurities. Such a filter is worse than useless since it soon becomes clogged and forms a breeding place for bacteria. In the *Pasteur filter*, however, the water is forced under pressure through a cylinder of unglazed porcelain. The bacteria and other impurities collect on the outside of the porcelain, which should be cleaned frequently and sterilized by heating to about 110°C . The Berkefeld filter (Fig. 61) is similar in construction. The same company makes an *army type filter* with which water from a stream may be filtered by the use of a small portable pump.

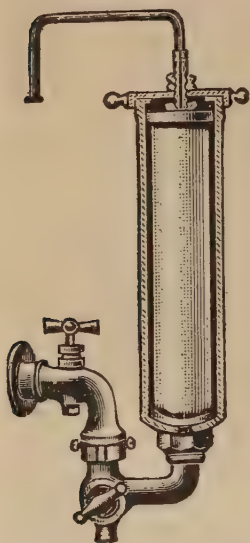


FIG. 61.—Porcelain Filter.

100. Aëration. Only surface water comes into contact with the oxygen of the air. When the water is agitated fresh portions are brought to the surface. In some reservoirs fountains have been installed which cause the water to spout up into the air and flow back over a large surface in thin layers. In some cases compressed air bubbles up through the water in the reservoir. In still other cases aëration is accomplished by letting the water flow over a series of cascades as it enters the reservoir. Aëration oxidizes organic matter and some of the bacteria are destroyed. Gases having disagreeable odors are also removed by this method of purification. See Fig. 62.

101. Light. Sunlight is useful in destroying bacteria. It is not very valuable for water purification, however, since it

does not penetrate the water to a very great depth. Thus only the surface layers are affected. Furthermore, light



FIG. 62.—Purification of water by aëration.

promotes the growth of algæ. We have already learned that it is desirable to have filtration beds covered, since algæ need light for their growth. To keep open reservoirs free from algæ costs cities a considerable sum each year.

102. Ultra-violet Rays.

If the sun's rays are passed through a prism and allowed to fall upon a screen, we can see a band of colors. See Fig. 63. A thermometer placed just beyond the red shows that heat rays are present,

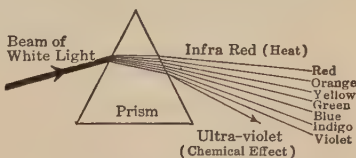


FIG. 63.—White light is split up into waves of different lengths.

although we can not see them. A photographic plate placed just beyond the violet is darkened by rays which are invisible, but very active chemically. These rays are known as *ultra-violet* light. They are very active in destroying bacteria. They can be prepared artificially by the use of incandescent mercury vapor inclosed in a *quartz* tube. They do not pass

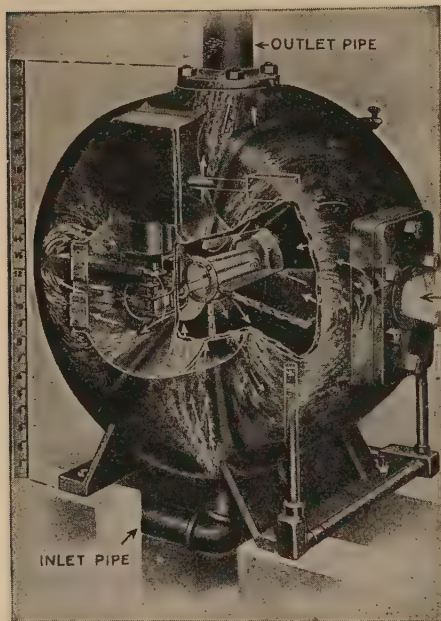


FIG. 64.—Phantom view of a water sterilizer.

through glass readily. Victor Henri showed that water exposed to ultra-violet light as it flows quite rapidly through the apparatus is rendered practically free from bacteria. Fig. 64 shows a phantom view of an ultra-violet sterilizer. Unfortunately quartz tubes have been very expensive, but it is hoped that the new methods of fusing quartz devised by Berry will cause the price to be somewhat reduced. The Uvi-

arc lamp (mercury vapor in quartz) burns the flesh, kills bacteria, causes colors to fade rapidly, and produces many other chemical effects by the action of ultra-violet rays. Fig. 65 shows a swimming pool equipped with ultra-violet sterilizers.

103. Boiling. In dry seasons when the water supply is low, people are warned to boil the drinking water. Very few bacteria can withstand a temperature of 100°C . for more than

a few minutes. The disease-producing bacteria are generally destroyed, especially if the boiling temperature is maintained for from 15 to 30 minutes. Of course this method is impractical for large-scale purification. The water has a flat taste after boiling, but if the water is subsequently aerated it becomes more palatable.

104. Cold. Many bacteria are destroyed at the freezing temperature of water. Ice is purer than the water from which it was obtained, probably



FIG. 65.—Swimming pool and sterilizers.

containing less than 5% as many bacteria. But if polluted water contains millions of bacteria per c. c., one would hardly care to use ice that contained 5% of that number. Ice for use internally should always be frozen from pure water, because some bacteria are not killed by the freezing temperature.

105. Use of Chemicals. One of the cheapest and one of the most effective methods of making drinking water wholesome is the use of chemicals to destroy bacteria.

1. *Ozone.* The use of ozone in purifying water was mentioned under our study of ozone. Its use is gaining favor, since it forms oxygen and an excess present in the water is not objectionable.

2. *Chlorin.* Probably no chemical is so widely used for purifying water as chlorin. It is not a difficult matter to liquefy chlorin gas, and several manufacturers can supply liquid chlorin under pressure in steel cylinders. It is then introduced into the water by letting it flow from these cylin-

ders. See Fig. 66. Sometimes the chlorin is obtained from sodium hypochlorite, or "chlorid of lime." In the nascent state chlorin is a very active germicide. It also decomposes some water in the presence of sunlight, thus setting free nascent oxygen. Chlorin is also useful in destroying algæ, but an excess of chlorin in water is objectionable, since it imparts to the water an unpleasant odor and a disagreeable taste.

3. *Copper Sulfate*. No chemical seems to be more effective in keeping city reservoirs free from algæ than copper sulfate.

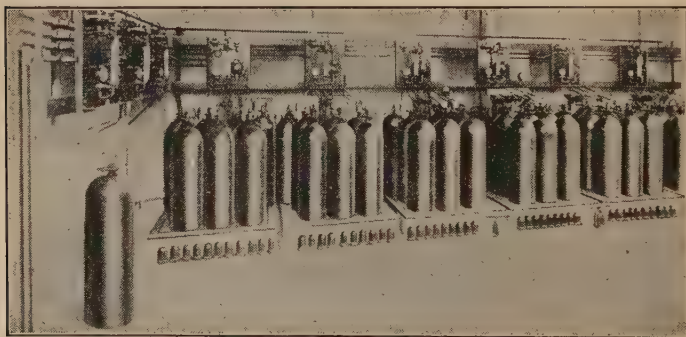


FIG. 66.—Rows of liquid chlorin cylinders.

It is also used as a germicide. So small an amount as 1 part in 10,000,000 parts of water is said to destroy typhoid bacteria and other disease-producing germs. Because it is known to be poisonous, there is considerable prejudice against its use. Used in such small quantities, however, there is no possible chance of any ill effects from its use for water purification.

106. Distillation. The only way to free water from non-volatile matter in solution is to evaporate the water and then condense its vapor. Such a method is known as *distillation*. When mineral matter in water interferes with its use for chemical or industrial purposes, it is necessary to distil the

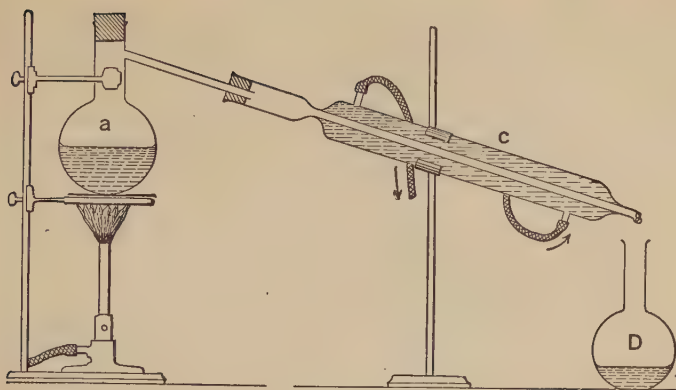


FIG. 67.—Apparatus illustrating distillation.

water. The water to be distilled is put in the distilling flask *a*, as shown in Fig. 67, and heated to boiling. The condenser *c* consists of two concentric tubes through the outer of which cold water flows continuously. The water vapor condenses in the inner tube and is collected in a receiver at *d*.

Water may be obtained in a reasonably pure state by distillation. Since any gases or volatile matter will readily be driven off by the heat, the first portion of the distillate should be rejected. The non-volatile matter remains in the distilling flask. Fig. 68 shows one type of continuous action still. The water that is used for condensation later flows into the still. Thus it is somewhat warmed by the heat of condensation.

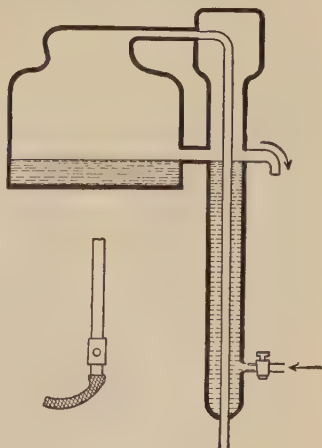
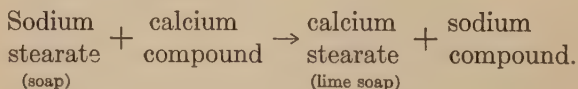


FIG. 68.—Continuous action still.

The student should not get the idea that distillation is used only for the purification of water. It is extensively used in purifying other liquids. In fact practically any liquid that does not decompose at the temperature of its boiling point may be purified in this manner. We define *distillation* as a process consisting of evaporation and subsequent condensation.

Liquids that have different boiling points may usually be separated by *fractional distillation*. To illustrate, petroleum is composed of several substances boiling at different temperatures. The petroleum is heated at a low temperature until the oils having a very low boiling point, such as naphtha, petroleum ether, gasoline, and benzine, are all volatilized and condensed. The temperature is raised until gas oil distillates are vaporized. At a still higher temperature various grades of lubricating oil and paraffin oil are obtained.

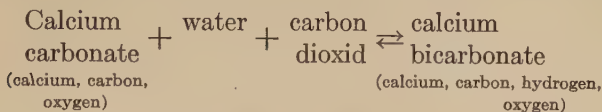
107. Hard Waters. The most common mineral matter found in hard waters consists of compounds of calcium, magnesium, and iron. When soap is added to a water containing a calcium compound, for example, the soap unites chemically with the calcium to form a gritty insoluble compound known as "lime soap."



Since this precipitate is formed by the union of the mineral matter with the soap, hard water is said to "curdle" soap. Magnesium and iron form similar insoluble compounds with soap. Soapsuds can not be formed in hard water until enough soap has been added to precipitate all the calcium and magnesium compounds that were present.

Waters that contain *bicarbonates* of calcium, magnesium, and iron are known as *temporary hard waters*. When water containing carbon dioxid in solution comes into contact with

limestone (calcium carbonate), the bicarbonate of calcium is formed as follows:



Calcium bicarbonate dissolves readily enough in water to make the water in limestone regions very hard. When water containing such a bicarbonate is boiled, the reaction is reversed. Carbon dioxid is driven off and the less soluble calcium carbonate comes down as a precipitate. Thus waters containing bicarbonates are called *temporary* hard waters because the mineral matter is precipitated when the water is boiled.

Permanent hard waters usually contain sulfates of calcium or magnesium. These substances are not precipitated when the water is boiled, although a slight amount of calcium sulfate may be thrown out of solution, since calcium sulfate is slightly less soluble in hot water than in cold water. Therefore the hardness is called *permanent*.

108. Objections to the Use of Hard Waters. 1. *Laundry Purposes.* If suds can not be produced until all the mineral matter in hard water is precipitated, evidently considerable soap will be wasted if hard water is used for laundry purposes. The gritty precipitate is objectionable too, since it accumulates on the sides of tubs and in the pores of the fabric, giving the garment a dingy appearance after washing.

2. *Steam Boilers.* Large quantities of water are evaporated to produce steam for power purposes. If hard water is used, its mineral matter remains after evaporation forming an incrustation known as "boiler scale." See Fig. 69. This



FIG. 69.—Pipe nearly closed by scale.

incrustation is a very poor conductor of heat and more fuel is needed to produce steam when even a thin scale is present. Engineers estimate that an incrustation of a magnesium compound $\frac{3}{64}$ in. thick requires 25% more fuel. The iron walls of the tubes are sometimes heated red hot and may collapse under the pressure of the steam.

Hard waters also produce corrosion or pitting in steam boilers, thus decreasing the life of the boiler or its flues. Dissolved oxygen and carbon dioxide are probably active in such corrosion.

3. *Other Industries.* Mineral matter is especially objectionable in water used in the dyeing industry. The color may be altered, or uneven dyeing or spotting may result, if hard water is used. Hard water may cause stains upon the leather in leather manufactures, or upon paper in the paper industry. In soap factories, sugar refineries, and chemical works hard water is objectionable. Automobile radiators soon lose in efficiency if the water used in them is very hard, and the water used in the storage batteries now so commonly used for automobiles and radio outfits must be free from mineral matter in solution.

109. Softening Hard Waters. Several compounds are used as water softeners. Slaked lime, sodium carbonate, and sodium aluminate are the most common softeners. *Slaked lime* is used to destroy "temporary hardness" in water without the expense of boiling. The precipitate formed soon settles. *Sodium carbonate* (washing soda) is inexpensive and it destroys hardness of both types. *Borax* is sometimes used about the household for softening water. It is too costly to be used on a large scale. Graphite, tannin, glue, etc., are sometimes added to water that is to be used for steam boilers. They do not prevent the formation of boiler scale, but they produce a softer scale which can be more easily removed by scraping.

Permutit is the name given to a compound manufactured

to soften hard waters. It is a sodium aluminum silicate that exchanges its sodium for the calcium and magnesium of hard waters. This granular compound is packed in large cylindrical tanks through which the water is filtered. See Fig. 70. As the water flows through the filter, it loses its calcium and

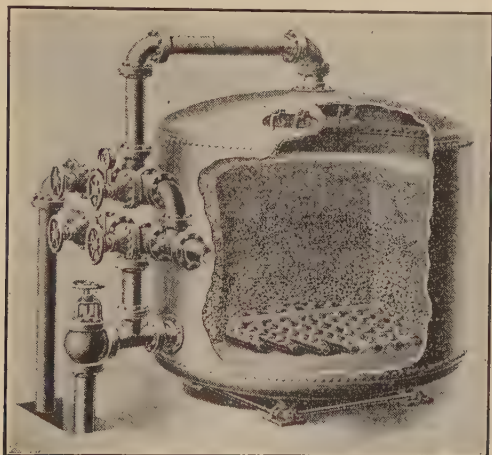
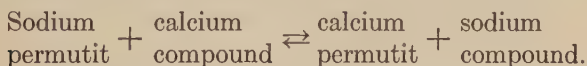


FIG. 70.—Water softener.

magnesium and takes up some sodium from the permutit. We may represent the reaction as follows:



When the permutit has lost all its sodium, it may be *regenerated* by letting it stand for several hours in the presence of a *concentrated* solution of common salt, sodium chlorid. The strong salt solution causes the above reaction to be reversed and the permutit is as good as before. *Decalco* is a similar compound which is manufactured by a different company. Such water softeners are also manufactured for use in dwelling houses.

SUMMARY

Impurities in water are: (1) *organic*, or (2) *inorganic*. They may be held in *suspension* or in *solution*.

Impurities in suspension may be removed as follows: (1) *sedimentation*; (2) *sedimentation with coagulum*; (3) *filtration*.

Organic matter including bacteria may be destroyed in several ways: (1) *aëration*; (2) *light*; (3) *ultra-violet rays*; (4) *boiling*; (5) *cold*; (6) *use of chemicals*.

Matter in solution in water may usually be removed by *distillation*. Liquids having different boiling points may be separated by *fractional distillation*.

Hard water contains mineral matter in solution. Very hard waters may contain several hundred parts per million. If the mineral matter is precipitated by boiling, the water is classed as *temporary* hard water. *Permanent* hard water can not be softened by boiling.

Hard waters waste soap, corrode boilers, produce boiler scale, and interfere in the manufacture of many different products.

Hard waters may be softened by using *sodium carbonate*, *lime*, *borax*, *permutit*, and *decalso*.

QUESTIONS

1. Distinguish between "pure water" and "wholesome water."
2. If you were making up solutions in the laboratory would you use filtered water or distilled water? Give reasons for your answer.
3. Why is a good microscope needed in a sanitary water analysis?
4. How would you test to determine the presence of mineral matter in solution in water?
5. Try to find out why water must be kept at the boiling temperature for some minutes to sterilize it.
6. How would you proceed to get pure water from water that contains both volatile and non-volatile matter in solution?
7. Why are small household filters apt to become a menace rather than a protection?
8. Is rain water suitable for use in storage batteries? Give a reason for your answer.
9. Bread is organic matter. Would it be objectionable in the water of a city reservoir? Explain.
10. If water "tends to purify itself upon freezing," is the ice obtained from the waters of a polluted stream suitable for use in iced tea? Explain.

CHAPTER XI

ATOMIC THEORY—ATOMIC WEIGHTS

110. Combining Weights. In the analysis of water we found that 1 part by weight of hydrogen combines with approximately 8 parts by weight of oxygen to form 9 parts by weight of water. If we analyze hydrogen chlorid, HCl , we find that in this case 1 part by weight of hydrogen combines with 35.5 parts of chlorin to form 36.5 parts by weight of hydrogen chlorid. Similar analyses show that:

1 gram of hydrogen combines with	4.66 gm. of nitrogen
1 gram of hydrogen combines with	3.0 gm. of carbon
1 gram of hydrogen combines with	16.0 gm. of sulfur.

Further study shows that these same elements, if they unite with each other, combine in the ratio of these weights just given. For example,

8 gm. of oxygen combine with	4.66 gm. of nitrogen
8 gm. of oxygen combine with	3.0 gm. of carbon
3 gm. of carbon combine with	16.0 gm. of sulfur
3 gm. of carbon combine with	35.5 gm. of chlorin.

These numbers just given show the ratio in which these elements combine. They are commonly known as *combining, or reacting weights*. We may use hydrogen as our standard; then the *combining weight of an element is the weight of that element which combines with one gram of hydrogen*.

Now the student can better understand just what Lavoisier did for chemistry when he introduced the use of the chemical balance. The manufacturer who wishes to make a chemical compound weighs out the different *factors* in the ratios of

their combining weights. For example, the combining weight of iron is 28, and the combining weight of sulfur is 16. Or, 28 parts of iron plus 16 parts of sulfur form 44 parts of iron sulfid. Suppose he heats 30 lb. of iron filings with 16 lb. of sulfur, he will also have 44 lb. of iron sulfid, but 2 lb. of iron will remain uncombined as waste.

Our grandmothers used to make their own baking powder by mixing 2 parts of cream of tartar with one part of baking soda. But when these compounds interact chemically, 188 parts by weight of cream of tartar react chemically with 84 parts by weight of baking soda. This is a ratio of 2.23 to 1, instead of 2 to 1. A large baking powder manufacturer using such a ratio would lose about 12% of the soda.

In a *substitution* reaction where one element *displaces* another, the ratio of the weights of the two elements that exchange places is exactly the same as their combining weights. For example,

23 gm. of sodium combine with	8 gm. of oxygen
23 gm. of sodium displace	1 gm. of hydrogen
12 gm. of magnesium combine with	8 gm. of oxygen
12 gm. of magnesium displace	1 gm. of hydrogen

Since the weight ratio is the same in all types of chemical reaction, *combining weights are often called reacting weights.*

Some elements have more than one combining weight. In water, the combining weight of oxygen is 8; in hydrogen peroxid it is 16. The higher combining weight is always a *multiple* of the lower. This is just what we would expect from a consideration of the law of multiple proportions, where two elements unite to form a series of compounds.

111. Atomic Theory. We have already learned that the *atom* is the unit used in chemistry. This conception of the atom is due to the experimental and theoretical work of John Dalton, who formulated his views in the *atomic theory*:

1. *Matter is made up of very small particles called atoms.*

2. *These atoms are indivisible by chemical means.* (See Chap. XXVI for modern view of matter.)

3. *The atom of an element has a definite weight.*

4. *The atoms of different elements have different weights.*

5. *Chemical affinity, or chemism, is the attraction between atoms.*

Just as a mason builds houses of many different designs by adding more bricks or by rearranging them, so the chemist builds thousands of compounds by adding, subtracting, or rearranging *atoms*. He has one advantage over the mason. His eighty-odd units vary in weight and properties, but he can not cut an atom into two parts by any known method. The reacting weights are always in a constant ratio. Thus it is easy to understand why the *law of definite proportion by weight* must be true. Adding an atom to a compound, or removing one from it, changes the weight of that compound by a *definite* amount.

In the compound water 2 atoms of hydrogen combine with 1 atom of oxygen; in the compound hydrogen peroxid, 2 atoms of hydrogen combine with 2 atoms of oxygen. In this series of compounds, the weight of hydrogen is constant (2 atoms); but in the second compound we have increased the weight by the addition of another oxygen atom. Therefore the weight of oxygen is doubled; it is a *multiple* of the weight of oxygen in the first compound. Thus if we accept the atomic theory, the law of multiple proportions follows logically.

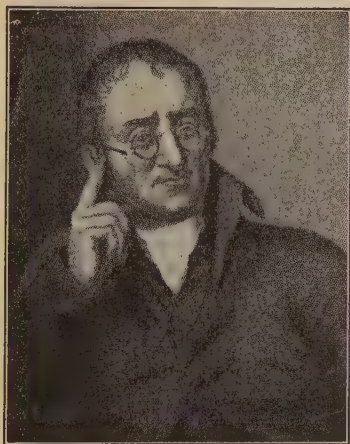
112. Atomic Weights. Atoms are too small to be weighed directly. Furthermore, the chemist is not interested in their *absolute* weight, but he is interested in their *relative* weight. He does not care whether the weight of the oxygen atom is one-millionth or one-billionth of a milligram, but it is of vital interest to know *how many times as heavy* oxygen is as some other atom. For comparison, some standard must be chosen. Both the hydrogen atom and the oxygen atom have been used as this standard. It is more *scientific* to use hydrogen

as the standard, because it is the lightest atom known. Suppose we call the atomic weight of hydrogen 1; then the atomic weight of oxygen would be 15.88, since the oxygen atom is 15.88 times as heavy as the hydrogen atom. Under the hydrogen standard, *the atomic weight of an element is that number which tells how many times as heavy its atom is as the hydrogen atom.*

For the sake of *convenience*, chemists always use the *oxygen* atom as the standard. Probably more than 50% of the compounds that the chemist analyzes contain oxygen, and few compounds contain hydrogen. The constant use of the number 15.88 is inconvenient. *Suppose we call oxygen 16 and make that the standard.* Then hydrogen would be $16 \div 15.88$, or 1.008. If oxygen is used as the standard, the atomic weights of a very large number of elements come out *approximate* whole numbers. This is another advantage in using the oxygen standard. All tables for atomic weights are based upon this standard. See inside of back cover. For use in solving problems, beginners may use the table of *approximate* atomic weights given on the inside of the front cover. It is unnecessary for students to memorize atomic weights.

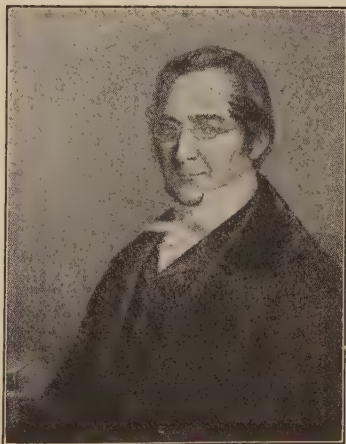
113. Chemical Formulas. We are now able to understand a fuller significance of chemical formulas: The formula, H_2O , represents: *a.* 1 molecule of water; *b.* it shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen; *c.* it represents 2 parts by weight of hydrogen (each atom of hydrogen having a weight of 1) and 16 parts by weight of oxygen; *d.* it stands for 18 parts by weight of water.

In any chemical formula the small number that follows any symbol shows the number of such atoms in the molecule. For example, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, the formula for cane sugar, shows that each molecule of sugar contains 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen. It also



John Dalton (1766–1844) was an English chemist and philosopher. He is best known in chemistry for his development of the atomic theory. He studied the absorption of gases by water and determined the composition of carbon dioxide. In the development of his atomic theory, Dalton stated the laws of definite proportion and multiple proportion.

Joseph Louis Gay-Lussac (1778–1850) was a distinguished French chemist. He was the first to announce that oxygen and hydrogen unite to form water in the simple ratio of one volume of oxygen to two volumes of hydrogen. Further investigations led to his discovery of the law of volumes for combining gases. He isolated boron and devised new methods of analyzing organic compounds.



signifies 144 (12×12) parts by weight of carbon, 22 (22×1) parts by weight of hydrogen, 176 (11×16) parts by weight of oxygen, and 342 parts by weight of sugar.

A number that precedes a formula shows the number of molecules used. For example, $5\text{H}_2\text{SO}_4$, stands for 5 molecules of sulfuric acid, each molecule containing 2 hydrogen atoms, 1 sulfur atom, and 4 oxygen atoms. The formula for copper nitrate, $\text{Cu}(\text{NO}_3)_2$, shows that each molecule contains 1 atom of copper, 2 atoms of nitrogen, and 6 atoms of oxygen. The formula is written $\text{Cu}(\text{NO}_3)_2$ instead of CuN_2O_6 , because the group of elements (NO_3) behaves like a single element.

114. Percentage Composition. If we know the formula of a compound and have a table of atomic weights, it is a matter of simple arithmetic to find the per cent of each element in that compound. First, *the molecular weight is equal to the sum of the weights of all the atoms in the compound.* Then we find what fractional part, or per cent, each element is of the whole molecule. Suppose we wish to find the percentage composition of potassium chlorate, KClO_3 . Using the table of atomic weights we find the following:

K, 1 atom.....	weight equals	39.0
Cl, 1 atom.....	weight equals	35.5
O ₃ , 3 atoms.....	weight equals	48.0 (3×16)
		molecular weight, 122.5

39, the weight of potassium $\div$ 122.5, total weight,
= 0.3183, equivalent to 31.83% potassium.

35.5, the weight of chlorin $\div$ 122.5, total weight,
= 0.2898, equivalent to 28.98% chlorin.

48, the weight of oxygen $\div$ 122.5, total weight,
= 0.3918, equivalent to 39.18% oxygen.

Often the compound contains water of crystallization. Sodium carbonate may be taken as an example of such a compound. Its formula is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The formula

PROBLEM: A compound contains carbon, 40%; hydrogen, 6.66%; and oxygen, 53.33%. Find its simplest formula. Let us tabulate our results as follows:

Element	Symbol	Per Cent	Atomic Weight	Per Cent Atomic Weight
Carbon.....	C	40.00	12	3.33
Hydrogen.....	H	6.66	1	6.66
Oxygen.....	O	53.33	16	3.33

To find the simplest ratio, we divide the quotients by the smallest quotient.

$$\begin{array}{r} 3.33 \overline{) 3.33 - 6.66 - 3.33} \\ \quad 1 \quad - \quad 2 \quad - \quad 1 \end{array}$$

The simplest formula of the compound is CH_2O .

PROBLEM: A compound contains carbon, 81.81%; hydrogen, 18.18%. Find its simplest formula.

Element	Symbol	Per Cent	Atomic Weight	Per Cent Atomic Weight
Carbon.....	C	81.81	12	6.82
Hydrogen.....	H	18.18	1	18.18

$$\begin{array}{r} 6.82 \overline{) 6.82 - 18.18} \\ \quad 1 \quad - \quad 2.66 \end{array}$$

Since there can be no fractional atoms, we find the simplest *whole number* ratio by clearing of fractions. Thus $\frac{3}{3}$ and $\frac{2}{3}$ have the ratio of 3 to 2. The formula is C_3H_2 .

To find the simplest formula of a compound: (1) *Divide the per cent of each element by its atomic weight*; (2) *Find the whole number ratio of these quotients*; (3) *Write the symbols of each element, using enough atoms to correspond with the ratio found*.

SUMMARY

The numbers which state the weight ratios in which elements combine are known as the *combining* weights of those elements. They are sometimes called reacting weights. Some elements have more than one reacting weight.

The *atomic theory* assumes:

1. That matter is made up of atoms.
2. These atoms are indivisible by chemical means.
3. The atom of an element has a definite weight.
4. Atoms of different elements have different weights.
5. Chemical affinity is the attraction between atoms.

The *atomic* weight of an element is that number which tells how many times as heavy its atom is as some standard atom, usually oxygen. The atomic weight of an element is either exactly equal to the combining weight or it is a multiple of it.

Chemical formulas show the composition of a compound. By use of a table of atomic weights, one may find the per cent of each element in a compound.

PROBLEMS

(Use Approximate Atomic Weights. See front cover.)

1. State fully the meaning of the following formulas: HNO_3 ; KCl ; $\text{Ca}(\text{OH})_2$; 4ZnCl_2 ; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{Ca}_3(\text{PO}_4)_2$.

2. What is the difference between $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and CuSO_4 ? How much weight would you expect the former to lose if heated to 100°C ?

3. Find the percentage composition of each of the following: Fe_2O_3 ; HgO ; $\text{Ca}_3(\text{PO}_4)_2$; NaCl ; $\text{Ca}(\text{NO}_3)_2$.

4. What per cent of sodium sulfate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is water?

5. Find the simplest formula of a compound containing carbon, 92.31%; hydrogen, 7.69%.

6. Find the simplest formula of a compound having the following composition: Sodium, 28.05%; carbon, 29.26%; hydrogen, 3.66%; and oxygen, 39.02%.

7. Analysis of a compound shows that it contains: Potassium, 39%; hydrogen, 1%; carbon, 12%; and oxygen, 48%. Find its simplest formula.

8. Find the simplest formula. Analysis: Carbon, 64.86%; hydrogen, 13.52%; oxygen, 21.62%.

9. Analysis: Nitrogen, 21.21%; hydrogen, 6.06%; sulfur, 24.24%; oxygen, 48.48%. Find simplest formula.

10. Analysis: Calcium, 19.32%; chlorine, 34.30%; oxygen, 46.38%. Find simplest formula.

11. Find the simplest formula for a compound having the following analysis: Phosphorus, 43.66%; oxygen, 56.33%.

12. A compound has the following composition: Iron, 70%; oxygen, 30%. Find its simplest formula.

13. Analysis: Hydrogen, 3.06%; phosphorus, 31.63%; oxygen, 65.30%. Find its simplest formula.

14. A compound is made up of the following elements: Sodium, 37.70%; silicon, 22.95%; oxygen, 39.34%. Find its simplest formula.

CHAPTER XII

GAS LAWS—MOLECULAR WEIGHTS

116. Gay-Lussac's Law. We have learned that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam. Further experiments show the following results concerning combining volumes of gases:

1 volume of hydrogen + 1 volume of chlorine $\rightarrow$ 2 volumes of hydrogen chloride.

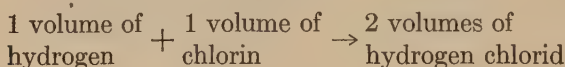
1 volume of nitrogen + 3 volumes of hydrogen $\rightarrow$ 2 volumes of ammonia.

The facts regarding *relative* combining volumes of gases were first summarized by Gay-Lussac in the law that bears his name: *The combining volumes of gases and the volume of the product, if it is a gas, may be expressed by small whole numbers.* This law applies only to gases. For example, (?) volumes of carbon + 4 volumes of hydrogen $\rightarrow$ 2 volumes of marsh gas. Carbon is not gaseous, therefore Gay-Lussac's law does not apply to it, and we do not know its combining volume in relation to hydrogen and to the product.

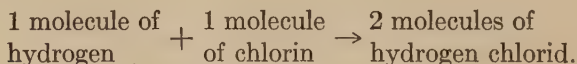
117. Avogadro's Law. We have now studied three gas laws, namely: the law of Boyle, the law of Charles, and the law of Gay-Lussac. Avogadro, an Italian chemist, made a careful study of the relationship between these laws and combining weights. Early in the nineteenth century he proposed the following theory: *Under the same conditions of temperature and pressure, equal volumes of all gases have the same number of molecules.* To illustrate, 1 liter of hydrogen has the same number of molecules as one liter of oxygen or any other gas at the same temperature and pressure. The actual number of molecules is of little importance, but

Avogadro's theory that the number is the same for all gases is very important. The theory was rejected by many of the chemists of Avogadro's time, but it is now known to be correct, since the actual number of molecules in one liter of a gas has been determined. We are justified now in calling this statement *Avogadro's Law*.

118. Molecules of Gaseous Elements Contain Two Atoms. Suppose we apply Avogadro's law to some of the results of Gay-Lussac's experiments. By experiment we have,

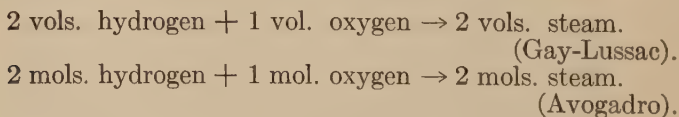


For the sake of simplicity let us assume that 1 volume contains a single molecule. Then we may re-write the above statement:



By analysis it may be learned that hydrogen chlorid has the formula HCl. Therefore each molecule of hydrogen chlorid contains one hydrogen atom. The hydrogen molecule from which we got enough hydrogen to form two molecules of hydrogen chlorid must have contained at least two hydrogen atoms. Similar reasoning shows that the chlorin molecule also contains two atoms.

From the equation for the formation of steam we may show that the oxygen molecule contains two atoms.



The formula H_2O shows us that each molecule of steam contains one oxygen atom. But we obtained enough oxygen

from one molecule to form two molecules of steam. Therefore the oxygen atom must have split up into two atoms.

Perhaps this relationship may be made clearer by using the larger circles in the following diagram to represent molecules and the smaller circles to represent the atoms as lettered. By Avogadro's law, the ratios are not affected when we use the

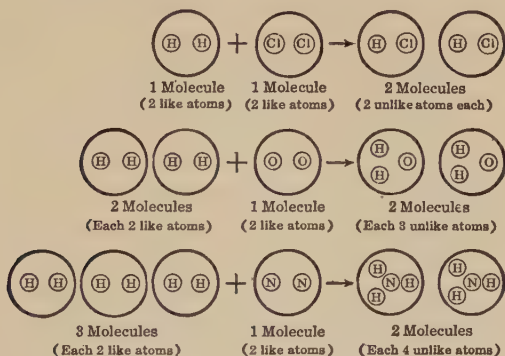
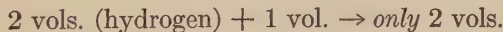


FIG. 71.—Elementary gases have two atoms in each molecule.

words “volume” and “molecule” interchangeably. See Fig. 71.

It is interesting to note that in the first equation, one volume of hydrogen plus one volume of chlorine form 2 volumes of hydrogen chloride. In the second case, however,



There is a contraction here because the new molecule that is formed contains *three* atoms instead of *two*. In the third case, we find 3 vols. and 1 vol. making only 2 vols., because the ammonia molecule (NH_3) contains *four* atoms. *No atoms are lost, and there is no change in weight, but the volumes vary because the atoms combine to form fewer molecules.*

In a similar manner it may be shown that *the molecules of all ordinary gaseous elements contain two atoms.* The mole-

cules of some elements that are liquid or solid at the ordinary temperature do not contain 2 atoms when they are vaporized. For example, mercury and iodine have at high temperatures only *one atom* to the molecule. Phosphorus has four; sulfur, 2, 4, or 8, varying with the temperature.

119. What is a Mole? If we weigh out enough grams of a substance to exactly equal its molecular weight, we have what is called by chemists *one mole* of that substance. *One mole of any substance is its molecular weight times 1 gram.* It is sometimes called *the gram-molecular weight of a substance*. For example, 1 mole of hydrogen is 2.016 grams. One mole of oxygen is 32 grams. One mole of hydrogen chlorid, HCl, is 36.5 grams ($1 + 35.5$). One mole of sulfuric acid, H_2SO_4 , is 98 grams ($2 + 32 + 64$).

120. How Much Space Does One Mole of a Gas Occupy? It is a little difficult to find the weight of a given volume of gas, but such experiments have often been performed. We know, for example, that one liter of hydrogen gas at standard conditions weighs almost 0.09 gm. How many liters of hydrogen are needed to weigh 2.016 gm.? Dividing 2.016 gm. by 0.09 gives *22.4 liters in one mole of hydrogen*. One liter of oxygen is found to weigh about 1.43 gm., and one mole of oxygen weighs 32 gm. $32 \div 1.43 = 22.4$, the number of liters one mole of oxygen will occupy at standard temperature and pressure.

From Avogadro's theory, we would expect that *a mole of one gas will occupy the same space as one mole of any other gas*. By laboratory test, it is found that the theory and facts agree in all cases. Therefore, *one mole of any gas occupies 22.4 liters of space at standard temperature and pressure*. This volume, 22.4 liters, is sometimes called the *gram-molecular volume*, since it is the volume of one *gram-molecule*.

121. Molecular Weight of a Gas, or of a Volatile Substance. If we know that one mole of any gas (S. T. P.) occupies 22.4 liters, it is an easy matter to find the molecular

weight of a gas or of any substance that vaporizes without decomposition. Suppose we construct a box which holds just 22.4 liters. See Fig. 72. Next let us weigh the empty box. If we then fill it at standard conditions with the vapor of the substance whose molecular weight is to be found, *the increase in weight in grams is the molecular weight of that substance.* In other words, *the molecular weight of a substance is the weight in grams of 22.4 liters of its vapor at standard conditions.*

It is not necessary to weigh exactly 22.4 liters of a gas to find its molecular weight. We may weigh 500 c. c., 1 liter, 10 liters, or any convenient volume and then compute the weight of 22.4 liters. For example, one liter of carbon monoxid, CO , weighs 1.25 gm. The weight of 22.4 liters equals 22.4×1.25 gm., or 28 gm. Therefore the molecular weight of carbon monoxid is 28.

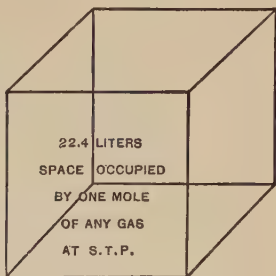


FIG. 72.—22.4 liter box.

It is not always practicable to weigh a gas at standard conditions. Of course any temperature and pressure may be used, because we can compute the weight at standard conditions by the use of the laws of Boyle and Charles.

122. To Find Weight of One Liter of any Gas. Sometimes students try to remember the weight of one liter of a gas as given in their text-book. If we know the formula of the gas, why not compute its weight from what we have learned in the preceding sections. For example, we wish to know the weight of 1 liter of sulfur dioxid, SO_2 . By adding the atomic weights, $32 + (2 \times 16)$, we find that the molecular weight is 64. One mole of sulfur dioxid equals 64×1 gm., or 64 gm. Then, 22.4 liters weigh 64 gm. We find the weight of one liter by dividing 64 gm. by 22.4. The weight is 2.85 gm. Since one liter of air weighs 1.29 gm., then sulfur

dioxid is about 2.2 times as heavy as air. *We find the weight of one liter of any gas by dividing its molecular weight in grams by 22.4 liters.* Since 22.4 liters of air weigh 28.95 gm., one can easily tell whether a gas is lighter than air or heavier by comparing its molecular weight with 28.95.

123. Molecular Weight of a Non-volatile Compound.

If a substance can not be vaporized, it is obvious that we can not find its molecular weight by the method given in section 121, but other methods are known for finding the molecular weight in such cases. We know that the addition of salt to water *lowers its freezing point and raises its boiling point.* Raoult found that if he dissolved one mole of alcohol, 46 grams, in one liter of water that the water would not freeze at 0°C . as before, but that the freezing point would be lowered 1.87°C . One liter of water containing one mole of solute freezes at -1.87°C . Further experiment shows that one mole of any substance, *except an acid, base, or salt*, lowers the freezing point 1.87°C . when added to 1 liter of water.

One mole of solute in 1000 grams of solvent is called a molar solution. Since a molar solution freezes at -1.87°C ., *to find the molecular weight of a substance we need only find by experiment the number of grams that must be dissolved in 1000 grams of water to lower its freezing point 1.87°C .* That number is the molecular weight.

Raoult also found that the molar solution of a *non-volatile* substance, acids, bases, and salts excepted, boils at a temperature 0.52°C . higher than that of the pure solvent. For example, if we dissolve 1 mole of sugar in 1000 grams of water, the solution will boil at a temperature of 100.52°C . Thus *we may find the molecular weight of a non-volatile substance by determining the number of grams that must be dissolved in 1000 grams of water to raise its boiling point 0.52°C .* The freezing point and boiling point methods of finding molecular weights give only approximate results as a rule.

If a substance is non-volatile and insoluble, no method of finding its molecular weight is known.

124. Correct Formulas. Students frequently ask why the formula for hydrogen peroxid is written H_2O_2 instead of HO , H_3O_3 , or some similar formula. The percentage composition from the formulas of HO , H_2O_2 , or H_3O_3 is the same in all cases. From the percentage composition we find that HO is the *simplest formula*. But to find which of the three formulas given above is the *correct formula*, we must find out whether the molecular weight is 17, 34, or 51. If it is found that the molecular weight of hydrogen peroxid is 34, then each atom of the formula HO must be taken twice to give that weight, and its formula is H_2O_2 .

PROBLEM: A compound contains carbon, 92.31%; hydrogen, 7.69%. One liter of its vapor at S. T. P. weighs 3.482 gm. Find its *correct formula*.

SOLUTION: By the method given in section 115 we first find its simplest formula, which is CH . If 1 liter weighs 3.482 gm., then 22.4 liters will weigh 3.482×22.4 , or 78 gm. The molecular weight of the compound is 78. But the molecular weight of the simplest formula is only 13, as we find by adding the atomic weights. Let x equal the number of times each element must be taken. Then $13x = 78$, and $x = 6$. It is obvious that each atom of the simplest formula must be taken 6 times to give the molecular weight, 78. The correct formula is C_6H_6 .

SUMMARY

Gay-Lussac's law states that the combining volumes of gases and the volume of the product, if it be gaseous, may be expressed by small whole numbers.

Avogadro's law assumes that equal volumes of all gases have the same number of molecules, the temperature and pressure being the same.

From Avogadro's law it may be shown that the *molecules of elementary gases contain 2 atoms*.

One mole of a substance is its molecular weight times 1 gram. One mole of any gas at S. T. P. occupies 22.4 liters. The weight of 22.4 liters of air is 28.95 gm.

To find the molecular weight of a volatile compound we find the

weight in grams of 22.4 liters of its vapor at standard conditions of temperature and pressure. The weight in grams is numerically equal to the molecular weight.

A *molar* solution contains 1 mole of solute per 1000 grams of solvent. One mole of solute in 1000 grams of water lowers its freezing point 1.87°C . and raises its boiling point 0.52°C . The molecular weight of a substance may be found by determining the number of grams needed to produce such a change in the freezing point and boiling point of a solution.

PROBLEMS

1. Prove that the nitrogen molecule contains 2 atoms.
2. Find the weight of 1 liter of hydrogen chlorid, HCl , in grams. Find the ratio of the weight of hydrogen chlorid to that of air.
3. Find the weight of 1 liter of the following gases: CH_4 ; NH_3 ; C_2H_2 ; CO_2 ; H_2S . Can you find the weight of 1 liter of common table salt, NaCl , by the same method? Explain.
4. One liter of chlorin at standard conditions weighs 3.17 gm. Find the molecular weight of chlorin.
5. At standard conditions 225 c. c. of sulfur dioxid weigh 0.6428 gm. Find its molecular weight.
6. Find the weight of 1 liter of water vapor, H_2O . Compare this weight with the weight of 1 liter of air. With the weight of 1 liter of liquid water.
7. The compounds, C_2H_6 , HBr , PH_3 , and N_2O are all gaseous at the ordinary temperature. Find the weight of 1 liter of each, and also find out how many times as heavy each one is as air.
8. A compound contains nitrogen, 30.51%; oxygen, 69.49%. 200 c. c. of the gas at S. T. P. weigh 0.817 gm. Find the simplest formula, the molecular weight, and the correct formula for this compound.
9. By analysis a compound is found to contain hydrogen, 5%; fluorin, 95%. 400 c. c. of the gas weigh 0.714 gm. Find the simplest formula, the molecular weight, and the correct formula for this compound.
10. One liter of alcohol vapor weighs 1.592 gm. at a temperature of 78°C . and under a pressure of 760 mm. of mercury. Find the molecular weight of alcohol. Hint. One liter of alcohol calculated at 0°C . weighs more than 1 liter at 78°C .
11. A compound shows the following analysis: Carbon, 32%; hydrogen, 4%; oxygen, 64%. Find its simplest formula. 15 gm. of this substance added to 1000 gm. of water lower its freezing point 0.187°C . Find the molecular weight and the correct formula.

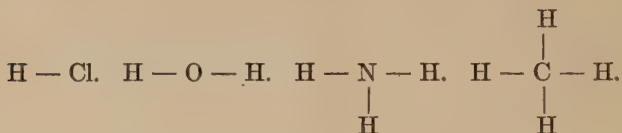
CHAPTER XIII

VALENCE

125. Introductory. The student has doubtless observed that we write the formula for hydrogen chlorid, HCl ; for water, H_2O ; for ammonia, NH_3 ; and for methane, CH_4 . Possibly he has wondered why this difference is made, and he may not find a very satisfactory explanation. But one atom of chlorin has the ability to hold *only* one hydrogen atom. An oxygen atom is capable of holding in combination *two* atoms of hydrogen; a nitrogen atom can hold *three* hydrogen atoms; and one carbon atom unites with *four* hydrogen atoms. The carbon atom has a greater *capacity* for holding hydrogen atoms than the oxygen atom. Crudely, we may say that its "grabbing power" is greater than that of the oxygen atom. Just as we have used the hydrogen atom here for comparison, so the chemist selects the hydrogen atom as the standard in the study of *valence*. *That property of an atom which indicates the number of hydrogen atoms with which it can combine or which it may displace is called its valence.*

126. Kinds of Valence. No compound is known in which the hydrogen atom ever combines with more than one atom of any other element. Hence hydrogen is taken as the standard in valence, and its atom is said to be *uni-valent*. Chlorin is also uni-valent, since one atom of chlorin combines with one atom of hydrogen. An element is said to be *bi-valent* if its atom combines with two atoms of hydrogen. Elements that have a valence of three are said to be *tri-valent*. An element having a valence of four is *quadri-valent*; one having a valence of five is *quinqvi-valent*; and one whose valence is six is called *hexa-valent*. No element is known that has a valence of more than eight. (*Octa-valent*.)

127. Theory of Valence. Just what the force is that holds one atom to another we do not know. It is a property of the atom, but we have already learned that it is usually impossible to *explain* properties. Various chemists have used different expressions, such as "bonds," "tubes of force," "links," "hooks," and "grabbing power" in their efforts to represent chemical affinity. Quite often the valence of an element is represented graphically as follows:



Each line or "bond" represents a valence of 1, and shows graphically that chlorine can hold 1 hydrogen atom; oxygen, 2; nitrogen, 3; and carbon, 4. The number of "bonds" an atom has tells us nothing concerning the *stability* of the compound it may form, but merely the number of atoms it *does* hold in that compound. For example, hydrogen and nitrogen have three valence "bonds," but the compound ammonia is not so stable as the compound HCl, where the number of "bonds" is one.

The modern theory of valence is that the force of attraction is electrical. J. J. Thomson suggests that certain elements, especially hydrogen and the metals, may *lose* one or more *electrons*, or *negatively charged particles*. On the other hand, oxygen and other non-metals are capable of *taking on* one or more electrons. Picture, if you will, atoms consisting of *protons* (positive charges of electricity) and *electrons*. Probably the greatest part of the atom is concentrated in a *nucleus*, which always contains more protons than electrons. Circulating around the nucleus in definite orbits are *external* electrons, in number just enough to neutralize the excess protons in the nucleus. Thus an atom that is free or uncom-



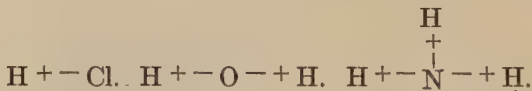
Sir Humphry Davy (1778–1829) was an English chemist and philosopher. He studied electrolysis, and by passing an electric current through fused substances and solutions, discovered several elements, including sodium, potassium, strontium, and magnesium. Davy discovered that nitrous oxid is an anesthetic. He proved that chlorin is an element, and showed that hydrogen chlorid is composed of hydrogen and chlorin. He is well-known as the inventor of the miner's safety lamp. In 1820 he was made president of the Royal Society of England.

Johann Jacob Berzelius (1779–1848) was a Swedish chemist. His work in analytical chemistry was so accurate that he discovered several elements, including cerium, selenium, and thorium. He determined the equivalent weight of many elements and improved analytical methods. He was the originator of the system of symbols used in chemistry.



bined does not show any electrical charge. Its valence is zero when it is uncombined.

The hydrogen atom has *one external electron* which it may lose under certain circumstances, thus leaving the hydrogen atom with an excess proton. Hydrogen atom — one electron = H^+ . The chlorine atom is believed to have 17 external electrons revolving around its nucleus, and to be capable of taking on one more. Chlorine atom + electron = Cl^- . It seems possible that the hydrogen which thus becomes positive will attract the negative chlorine to form a molecule of hydrogen chloride, HCl . For example, $H^+ + Cl^- = HCl$. An atom that can lose two electrons, calcium (Ca^{++}) for example, has a positive valence of 2; an atom, oxygen ($O^=$) for example, that can gain two electrons has a negative valence of 2. The aluminum atom can lose three electrons, thus giving it a positive valence of 3. The following formulas show graphically the electrical conception of valence:



But it does not matter so much after all whether we know “why” or “how” atoms unite. The fact that they *do* unite is more important. The scheme of valence is a valuable working tool for the chemist. He learns the valences of the important elements instead of trying to memorize the formulas for thousands of compounds. Knowing the valence, he can write formulas for compounds, even for those with which he is unfamiliar.

128. Valence of Elements in Binary Compounds. If an element unites with hydrogen to form a binary compound we can easily tell its valence. We learned that chlorine is univalent, since it combines with hydrogen atom for atom. Oxygen is bivalent, since one oxygen atom holds two hydrogen

atoms. In the same manner we learned that nitrogen has a valence of 3, and carbon a valence of 4.

Some elements do not combine with hydrogen directly, but such elements almost always unite with oxygen. Thus oxygen may be used as a standard in such cases. Examples of such compounds include Na_2O , CaO , Al_2O_3 , and SnO_2 . Since it takes two atoms of sodium to unite with one atom of bivalent oxygen, sodium must have a valence of one.

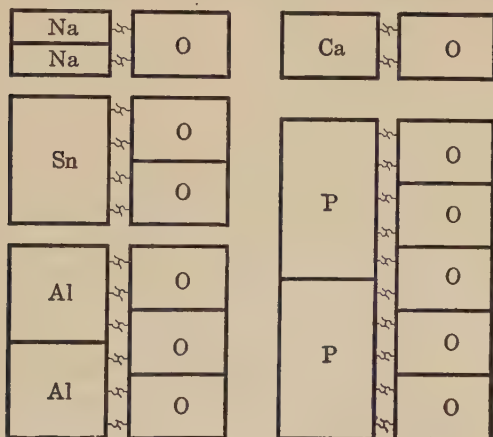


FIG. 73.—Blocks show valence.

We conclude that the valence of calcium is two, since it unites with oxygen atom for atom. Aluminum, Al, is 3; and tin, Sn, is 4. Sometimes valence blocks are used to show valence more clearly. See Fig. 73.

In any *binary compound*, the total number of "bonds" of the positive atoms must exactly equal the total number of "bonds" of the negative atoms. To illustrate, we may use the formula Al_2O_3 . Let us write the symbol of each element, using accent marks to indicate its valence as follows: $\text{Al}''' \text{O}''$. The elements can not combine atom for atom. We see at a glance

that 6 is the smallest multiple of both 2 and 3. Each element must have a total of six "bonds." Therefore we shall need 2 aluminum atoms of 3 "bonds" each and 3 oxygen atoms of 2 "bonds" each. Thus we find the formula for aluminum oxid to be $\text{Al}_2''' \text{O}_3''$. *The product of the number of atoms of one element times its valence equals the product of the number of atoms of the other element times its valence.*

Some students learn more quickly the following method of criss-crossing valences: $\overset{\text{III}}{\text{Al}}_2 \overset{\text{II}}{\text{O}}_3$ or $\overset{\text{II}}{\text{P}}_2 \overset{\text{III}}{\text{O}}_3$. The valence and the number of atoms needed to balance the compound are just reversed. By the use of this method we get $\overset{\text{IV}}{\text{Sn}}_2 \overset{\text{II}}{\text{O}}_4$ instead of SnO_2 . When the numbers are *even* we must simplify by reducing the numbers to their lowest terms.

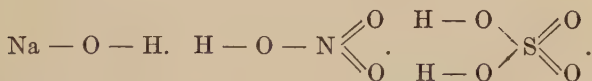
If the student looks up the valence of the elements (inside front cover) he should be able to write the formula for any oxid. For example, magnesium has a valence of 2. Therefore the formula for its oxid is MgO , not Mg_2O_3 , Mg_2O , or MgO_2 . In the same manner, keeping in mind the fact that the valence of chlorine in chlorids is one, we write NaCl , MgCl_2 , AlCl_3 , and SnCl_4 .

129. Valence of Radicals. It would seem as if the valence might be more difficult to determine when there are three or more elements in a compound. This may be true, but in the majority of such cases two of the elements in such a compound form a *radical*. In a radical two or more elements may act as one. *A radical may be defined as a group of elements that generally acts as a single element.* In the compound sodium hydroxid, NaOH , the group (OH) is a radical. In sulfuric acid, H_2SO_4 , the (SO_4) group is a radical. The compound nitric acid, HNO_3 , contains the radical (NO_3) . Since in a radical the two elements act like a single element, we can find the valence of a radical in exactly the same manner as we determined valence of elements in binary compounds.

For example the (OH) radical has a valence of 1; the (SO₄) group has a valence of 2, since it unites with 2 atoms of hydrogen; the (NO₃) group has a valence of 1.

Suppose we desire to write hydroxids of the metals whose valence we learned in section 128. Calcium hydroxid is Ca(OH)₂; aluminum hydroxid, Al(OH)₃; and tin hydroxid, Sn(OH)₄. For sulfates of these metals we write Na₂SO₄, CaSO₄, Al₂(SO₄)₃, and Sn(SO₄)₂.

That the oxygen in a ternary compound usually holds in combination all the other elements may be seen from the following structural formulas:

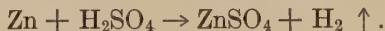


The student will soon learn the valence of the more common radicals. The majority of them combine with hydrogen, and their valence can be found from some formula with which the student is familiar. For example, no one can forget that the formula for sulfuric acid is H₂SO₄. Then he can apply this knowledge to the dozen or more sulfates he may study, all of which have one or more sulfate (SO₄)" radicals.

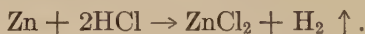
130. Variable Valence. It would be easier if no element ever varied in its valency. But some elements are quite fickle. For example, the mercury atom (Hg) may lose one electron and have a valence of one, as in the compound HgCl, mercurous chlorid. Under different conditions, it may lose two electrons and have a valence of two as in the compound HgCl₂, mercuric chlorid. Iron forms two oxids: *ferrous* oxid, FeO, in which the valence of the iron is 2; and *ferric* oxid, Fe₂O₃, in which the valence of the iron is three. The valence of a few elements never appears to vary. But a review of the table inside the front cover shows that several elements vary considerably. Such elements can form more different compounds. If the valence of a metal varies, the

metallic element takes the ending *ous* in its lower valence compound, and the ending *ic* in that of higher valence. Cuprous oxid, Cu_2O ; cupric oxid, CuO .

131. The Relation of Valence to Substitution. Just as it is impossible to have 1 atom of a bivalent element combine with 1 atom of a univalent element, so do we find it impossible to substitute 1 bivalent atom for 1 univalent atom. When we try to substitute zinc for the hydrogen in sulfuric acid, 1 bivalent zinc atom takes the place of 2 hydrogen atoms. We may write the following equation:



If we are writing the equation for the action of hydrogen chlorid on zinc, it requires two molecules of hydrogen chlorid to supply the two atoms of hydrogen that can be replaced by the bivalent element zinc.



132. Some Apparent Exceptions. The beginner may be disposed to expect too much from the scheme of valence. He can of course write formulas for compounds that do not exist. By the use of valence, for example, he might balance compounds to represent sulfates for each element, only to learn that all elements do not form sulfates. Then the student will find many compounds that are very puzzling, such as H_2O_2 , CaC_2 , Fe_3O_4 , C_2H_2 , and Pb_3O_4 . He will find valence helpful in many ways, but he must not expect it to prove a panacea for all the ills of the chemist.

133. Table of Valences. To familiarize the student with the valences of the most common elements, a table is given here for use in the problems at the end of this chapter. The elements having a variable valence appear in two or more columns. In writing formulas it may help the beginner

balance the compound if he writes after each element or radical an accent mark ('), to indicate its valence.

EXAMPLES: $\text{Ca}''(\text{CO}_3)'$; $\text{As}_2''' \text{S}_3''$; $\text{Mg}''\text{O}''$; $\text{P}_2''''\text{O}_5''$.

TABLE OF VALENCE

One	Two	Three	Four	Five	Six
Cl, H, I, Hg, Ag, Na, K	Ca, Cu, Fe, Mg, Hg, O, Sn, Zn, S	Al, Fe, N, P	C, Si, S, Sn	N, P	S

VALENCE OF COMMON RADICALS. (All but one are negative radicals)

One	Two	Three
OH, NO_3 , ClO_3 , NH_4 (positive), NO_2 , MnO_4	SO_4 , CO_3 , SO_3 , CrO_4	PO_4 , PO_3 , BO_3

QUESTIONS

1. Write the formulas for the oxids of the following metals: K, Cu, Mg, Ag, and Zn.
2. Write two oxids for the following elements: Fe, Sn, Hg, N, and P.
3. Write the formulas for the hydroxids of all the elements given in question 1.
4. Write the formulas for two sulfates of the following: Fe, Sn, and Hg.
5. Write the formulas for the sulfate, nitrate, chlorid, hydroxid, and phosphate of ammonium, NH_4 .
6. Write the formulas for the permanganates (MnO_4) of sodium and potassium.
7. In what two ways can you determine the valence of a radical?
8. In the top row of the following table certain elements and radicals are given with their valence indicated. In the left-hand

column a number of metals are listed. Fill in the table for all the metals in the same manner as for the sodium compounds.

	Oxids	Hy- droids	Chlorids	Nitrates	Sulfates	Phos- phates	Car- bonates
	O''	(OH)'	Cl'	(NO ₃)'	(SO ₄)''	(PO ₄)'''	(CO ₃)''
Na'	Na ₂ O	NaOH	NaCl	NaNO ₃	Na ₂ (SO ₄)	Na ₃ (PO ₄)	Na ₂ (CO ₃)
K'							
Hg'							
Ag'							
Ca''							
Cu''							
Fe'''							
Mg''							
Al'''							
Pb''							
Fe''							
Zn''							
Sn'''							

CHAPTER XIV

CHEMICAL EQUATIONS

134. Equations. As a matter of convenience chemists use equations to show what *does* take place during a chemical reaction. On the *left* side of the equation we write the formulas of all the *factors*, or of all the elements and compounds we use in beginning the experiment. On the *right* side of the equation we write the formulas of all the *products* that are left when the experiment is completed. A formula equation has the advantage over a word equation, since it is more explicit and considerably briefer. *A chemical equation is not a prophecy but a statement of fact.* It shows what actually does happen.

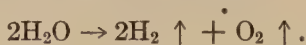
A chemical equation must be correct in three particular respects: 1. *It must represent the facts;* 2. *Every compound in the equation must be balanced as to valence;* 3. *There must be the same number of atoms on both sides of the equation.* Before one can write an equation, he must know all the *factors* and all the *products*. This means he must know with what chemicals he started, as well as those that are left at the end of the reaction. Analysis is the only way in which such facts are determined. To finish the second step in writing equations, *one must know the valence of each element.* Then he can balance each compound correctly. The third step is a matter of simple arithmetic. No matter is gained or lost during the reaction, so the student must count to see that there is the same number of atoms on the left side of the equation that there is on the right side.

135. Type Equations. Since one learns by doing and by example, let us study some of the equations where the facts

have already been learned. We decomposed water to prepare hydrogen and oxygen. Water is the only factor, and the products are hydrogen and oxygen. Thus we write,



Such an equation appears to be correct, but we have forgotten just one thing. *The molecule of an elementary gas contains two atoms.* To get two atoms of oxygen, we must use two molecules of water; in other words, the above equation must be multiplied by two throughout.



This equation is correct in every respect. Decomposing mercuric oxid, HgO , we have the following:



But here again we must double each compound and element to form the *molecular* equation,

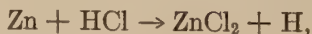


Let us next take up the study of an equation where substitution occurs. When hydrogen chlorid is added to zinc, the zinc displaces the hydrogen which is set free. Zinc chlorid is the other product that is formed. If we write the equation as shown below,



a little study shows that it is incorrect. It appears correct as to fact, but zinc is bivalent. Therefore ZnCl_2 is the formula for zinc chlorid.

Writing the equation,



we find that the facts are represented and that every compound is correct as to valence. But there are more atoms on the right side than on the left. We need *one more chlorine atom*. We must not write HCl_2 to remedy this need because hydrogen has a valence of one only and it can not hold two chlorine atoms. One of the most common mistakes made by the beginner is that of spoiling a balanced compound in order to get the required number of atoms. In this case as well as in all others *we may use as many molecules as we need*. By using 2 molecules of hydrogen chlorid, 2HCl , our equation becomes,



This equation states the facts, every element has the correct valence, no atoms have been gained or lost, and the hydrogen molecule (elementary gas) has two atoms.

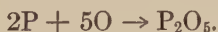
The equation for the decomposition of potassium chlorate, KClO_3 , follows:



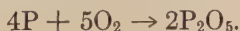
Doubling to get two atoms for each oxygen molecule, we have the correct equation,



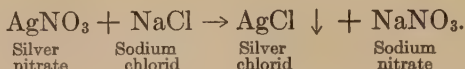
When phosphorus burns, it combines with oxygen to form the oxid P_2O_5 . We first write the equation as follows:



But we have only five atoms of oxygen, enough to make $2\frac{1}{2}$ molecules of two atoms each. But we do not represent half molecules, so here again we must multiply the above equation by two to make it correct.



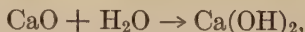
The following equation is an example of metathesis:



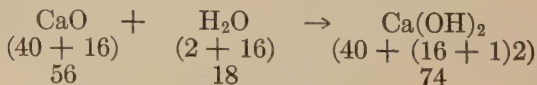
It is customary in writing formulas to write the electro-positive element first. This is usually either hydrogen or some metal. We would hardly expect two positive elements to unite chemically, nor two negative elements, since charges of like sign repel. In the above equation the silver (+) takes the place of the sodium (+), and unites with the chlorine (—); the sodium unites with the (NO₃) radical, which is negative. We may be pretty certain that in double substitution a metallic element will be substituted for another metallic element and combine with a non-metal or a non-metallic radical. *Radicals usually remain intact during chemical reactions.*

CHEMICAL ARITHMETIC

136. Problems Relating to Equations. *a. Weights given and weights required.* Since chemical equations show the number of atoms taking part in a chemical reaction and atoms have definite weights, the relative weights of factors and products may be easily calculated. In the equation,



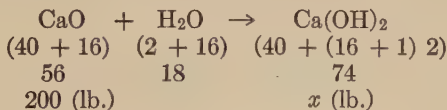
we see that one molecule of calcium oxid unites with one molecule of water to form one molecule of calcium hydroxid. Let us write below the formula of each compound the atomic weight of each element taken as many times as the atom appears in the formula. For example:



It is evident that 56 parts by weight of calcium oxid unite with 18 parts by weight of water to form 74 parts by weight of calcium hydroxid. If we start with 56 lb. of calcium oxid, then 74 lb. of calcium hydroxid are formed. If we start with grams or ounces, then the result will be in grams or ounces.

PROBLEM: Given 200 lb. of calcium oxid. How many pounds of calcium hydroxid can be formed by the addition of water?

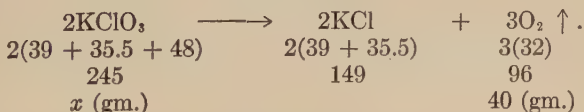
SOLUTION: Under the equation let us write the molecular weights as found by *adding* (*never by multiplying*) the atomic weights. Then let us write the actual weight of each compound under the molecular weight of that compound, as follows:



By proportion, $56 : 74 = 200 : x$; whence, $x = 264.3$ lb. of calcium hydroxid. The student should observe that MOLECULAR WEIGHT OF KNOWN COMPOUND : MOLECULAR WEIGHT OF UNKNOWN COMPOUND = ACTUAL WEIGHT OF KNOWN COMPOUND : ACTUAL WEIGHT OF UNKNOWN COMPOUND. The amount of water needed was not a part of the problem, therefore we do not use the molecular weight of water at all.

PROBLEM: How many grams of potassium chlorate must be used to prepare 40 grams of oxygen?

SOLUTION: Let us first write the equation with the atomic weights.



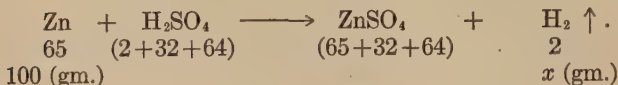
By proportion, $245 : 96 = x : 40$; whence, $x = 102.1$ gm. We do not use the number 149, unless we wish to find the weight of potassium chlorid.

b. Weights given and volumes required. Problems of this type are not so common as those we have just studied, but

quite often we need to know how many liters of a gas are liberated by a given weight of material.

PROBLEM: How many grams of hydrogen will be liberated by the action of 100 gm. of zinc on an excess of sulfuric acid? How many liters will the hydrogen occupy at standard conditions?

SOLUTION:

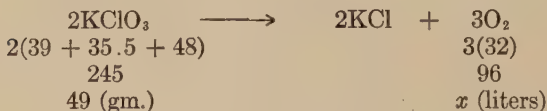


By proportion, $65 : 2 = 100 : x$; whence $x = 3.08$ gm.

Since 1 liter of hydrogen weighs 0.09 gm., 3.08 gm. will occupy as many liters as $3.08 \div 0.09$. The answer is 34.2 liters.

PROBLEM: How many liters of oxygen can be prepared by heating 49 gm. of potassium chlorate?

SOLUTION:



We find by inspection that 245 gm. of potassium chlorate yield 3 moles of oxygen. One mole is 22.4 liters, and 3 moles would occupy 67.2 liters. Let us substitute for 96 gm. its equivalent, 67.2 liters. Then by proportion, $245 : 67.2 = 49 : x$; whence, $x = 15.64$ liters. In all equations of this type WE MAY SUBSTITUTE FOR MOLECULAR WEIGHT IN GRAMS 22.4 LITERS FOR EVERY MOLE REPRESENTED AND THEN SOLVE BY SIMPLE PROPORTION. This method applies to *gases only*.

c. Volumes Given and Volumes Required. The theory of Avogadro simplifies problems in chemistry that deal with volume relations. If we write the molecular equation first then we can use the coefficients, which represent the number of molecules taken, as numbers to show the volume ratios of gases.

PROBLEM: How many liters of oxygen will be required for the combustion of 14 liters of hydrogen?

SOLUTION: $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$.

Whence 2 vols. + 1 vol. $\rightleftharpoons$ 2 vols. H_2O (vapor) by Avogadro.
14 vols. x vols.

By proportion, $2 : 1 = 14 : x$. Whence, $x = 7$, the number of liters of oxygen required.

PROBLEM: How many liters of oxygen are needed for the complete combustion of 12 liters of marsh gas, CH_4 ?

EQUATION: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 \uparrow + 2\text{H}_2\text{O}$.

1 vol. 2 vols. 1 vol. 2 vols. (vapor)
12 l. x l.

By proportion, 1 vol. : 2 vols. = 12 liters : x liters. Whence $x = 24$ liters. By analysis, if one vol. of CH_4 unites with 2 vols. of oxygen, we will need 24 liters of oxygen to unite with 12 liters of CH_4 .

EQUATIONS

(For reference and for use in solving problems)

- $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 \uparrow$.
- $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$.
- $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \uparrow$.
- $\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \uparrow$.
- $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$.
- $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \uparrow$.
- $2\text{C}_2\text{H}_2 + 5\text{O}_2 \rightarrow 4\text{CO}_2 \uparrow + 2\text{H}_2\text{O}$.
- $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + \text{H}_2\text{O}_2$.
- $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CaH}_2(\text{CO}_3)_2$.

PROBLEMS

(Use approximate atomic weights)

- How many grams of oxygen can be prepared from 10 gm. of mercuric oxid?
- How many grams of oxygen can be prepared from 10 gm. of potassium chlorate? How many liters does this oxygen occupy?
- How many grams of zinc are needed to liberate 5 grams of hydrogen from sulfuric acid? How many grams of zinc would be needed to liberate 5 liters of hydrogen?
- How many grams of sodium chlorid, NaCl , are needed to unite with 10 gm. of silver nitrate, AgNO_3 , in water solution? How

many grams of silver chlorid will be precipitated? If the excess water is evaporated, how many grams of sodium nitrate will be left?

5. How many liters of hydrogen will be needed to reduce 10 gm. of copper oxid to metallic copper?

6. How many grams of potassium chlorate are needed to prepare 9 moles of oxygen? To prepare 22.4 liters of oxygen?

7. How many pounds of copper can be obtained from 200 lb. of copper oxid?

8. How many pounds of copper sulfate can be made from 300 lb. of copper?

9. How many liters of oxygen are needed to burn 5 liters of acetylene? How many liters of carbon dioxid will be formed?

CHAPTER XV

THE ATMOSPHERE

A. THE AIR

137. Introductory. While the terms "air" and "atmosphere" have a slight difference in meaning, they are often used interchangeably. We have spoken of the importance of the air in our discussion of oxidation and combustion. We know that a part of this colorless, odorless, tasteless gas that we call "air" is oxygen. It can not be composed wholly of oxygen, however, since pure oxygen is much more active. Then, too, one liter of air weighs 1.29 gm., considerably less than the weight of one liter of oxygen. Compared with the weight of one liter of water, 1000 gm., air seems very light and the expression "as light as air" is a common one. Although air is only about $1/773$ as heavy as water, yet a good-sized schoolroom contains several hundred pounds.

138. Constituents of the Air. In addition to oxygen, the air contains *nitrogen, argon, carbon dioxid, water vapor, and several rare gases*. Since other gases are naturally escaping into the air, *traces* of hydrogen sulfid (H_2S), sulfur dioxid (SO_2), ammonia (NH_3), and other gases are present in certain localities. Ozone is formed in small quantity during thunderstorms. Particles of dust, bacteria, and smoke are always present in the air. The average per cent of the more important constituents by volume is as follows:

	Per cent
Oxygen.....	21
Nitrogen.....	78
Carbon dioxid.....	0.04
Argon.....	0.94
Water vapor, varies from a small fraction to as high as 2%	

139. Air is a Mixture. Several proofs may be given that air is a mixture and not a chemical compound.

1. The composition of the air varies slightly in different localities, and in the same locality at different times. We know that a compound always has a definite composition.

2. If we mix the constituents in the same proportion in

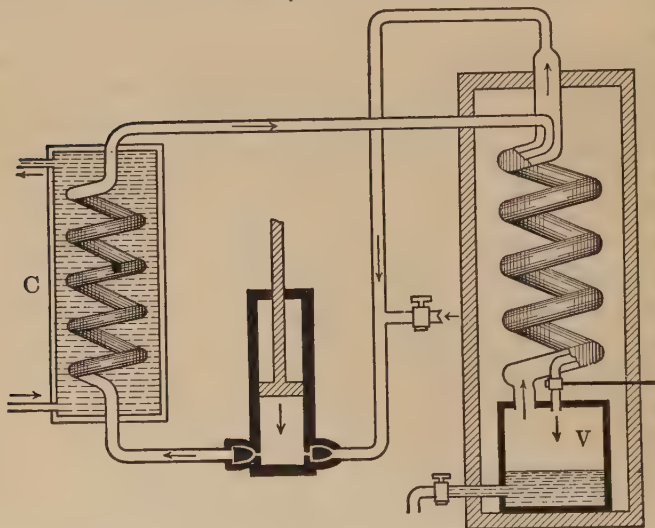


FIG. 74.—Linde's apparatus for liquefying air.

which they are found in air, there is no evidence of any chemical action, such as the evolution of heat and light.

3. If we dissolve a compound its definite composition is not in any way changed. But if we analyze air that has been dissolved in water, we find that it is more than one-third oxygen instead of one-fifth. Therefore air dissolves as a mixture.

4. A compound has a definite boiling point. If we let liquid air boil, the nitrogen evaporates first leaving nearly pure liquid oxygen.

Other proofs might be given to show that air is a mixture and not a compound, but these four are quite enough to convince the most skeptical.

140. Liquid Air. If we open the valve of an inflated tire and hold one hand in the escaping air, we notice a marked cooling effect. *Cooling always occurs when gases expand.* As they are compressed, heat is produced. To liquefy

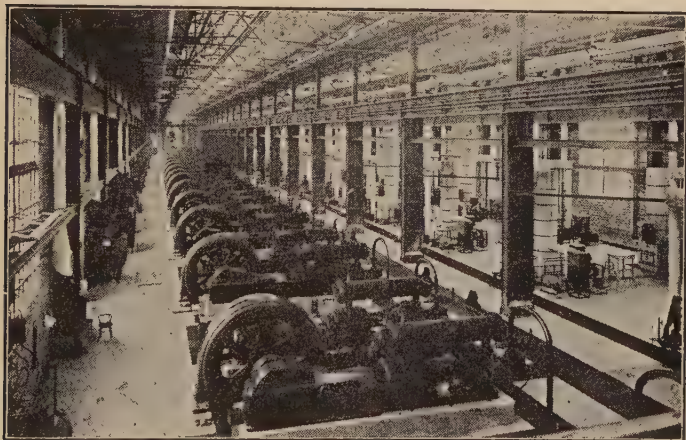


FIG. 75.—Compressors for making liquid air.

gases we first compress them and absorb the heat of compression by cold water. Then the gases are permitted to expand to cool them to a low temperature. In making liquid air, a pressure of 3000 or 4000 lb. to the square inch is used; after the heat is absorbed in the pipes of *C*, Fig. 74, the air then escapes through a needle valve at *V* in the inner of two concentric pipes. The escaping air in the liquefier is led back around the compressed air in the inner pipe, thus cooling it before it escapes. This process is repeated until a temperature is reached at which some of the air liquefies as it escapes through the needle valve. Fig. 75 shows a large number of

compressors for use in making liquid air at the Government plant at Muscle Shoals, Alabama.

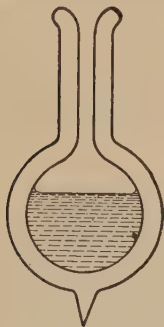


FIG. 76.—Dewar flask, cross-section.

141. Properties of Liquid Air. Liquid air is nearly colorless. Under ordinary atmospheric pressure it boils at about -190° C. Of course it is a mixture of oxygen and nitrogen. The nitrogen, which boils at a lower temperature than the oxygen, evaporates first; the temperature then rises gradually. Finally a blue liquid, containing about 90% oxygen is left. The temperature is so low that alcohol and carbon dioxid solidify in liquid air. Mercury is frozen so hard

that it can be used as a hammer to drive nails. A rubber ball thrown into liquid air and then on the floor breaks as if it were made of glass. Tin becomes brittle and lead elastic when immersed in this cold liquid. A piece of ice thrown into liquid air will make it boil vigorously because the ice is so hot in comparison. If we stop to think that boiling water is only 100 Centigrade degrees hotter than ice, and that ice is about 190 Centigrade degrees hotter than liquid air, we get a better idea of the low temperature of liquid air.

Dewar devised a flask for keeping liquid air. Fig. 76 shows that it is a double-walled container; the space between the two walls is a vacuum. Since a vacuum is a non-conductor of heat and since the glass is silvered to prevent the transmission of radiant heat, liquid air keeps fairly well inside such a flask, as it boils quite slowly. The thermos bottle is constructed on the same principle. See Fig. 77.



FIG. 77.—Thermos bottle.

142. Uses for Liquid Air. Liquid air is used to produce very low temperatures. We have already learned that it is a source of oxygen for commercial use. The nitrogen which boils off first finds use in filling electric bulbs and for making nitrogen compounds to be used either for fertilizer or in the manufacture of explosives.

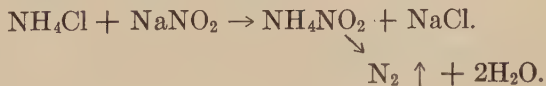
B. NITROGEN

143. Preparation of Nitrogen. 1. *From Air.* It is possible to get a mixture of gases largely composed of nitrogen by removing all the oxygen from air. The oxygen may be removed in several ways such as passing air over hot copper, or by introducing phosphorus to combine with the oxygen. If we ignite a piece of phosphorus in a small crucible floating on water and cover it with an inverted bottle of air, the phosphorus combines with the oxygen to form phosphorus pentoxid. As the pentoxid dissolves the water rises in the bottle taking the place of the oxygen which was removed. The bulk of the remaining gas is nitrogen.

2. *From Ammonium Nitrite.* Pure nitrogen may be obtained by heating ammonium nitrite, NH_4NO_2 , a compound that decomposes into water and nitrogen as follows.



In actual practice the decomposition of the ammonium nitrite is too rapid and the gas is prepared by heating a mixture of ammonium chlorid and sodium nitrite. These two compounds form ammonium nitrite which in turn yields the nitrogen. The equation is as follows:



144. Properties of Nitrogen. 1. *Physical.* Nitrogen is a colorless, odorless, tasteless gas. It is slightly lighter than

air and slightly soluble in water. Nitrogen is not poisonous but animals die in nitrogen from oxygen starvation. The fact that a live mouse soon died when put in a jar of nitrogen was first observed by Rutherford who discovered this gas in 1772. For this reason the gas was named *azote* (not capable of sustaining life) by Lavoisier. Like oxygen and hydrogen, nitrogen is rather difficult to liquefy.

2. *Chemical*. Nitrogen is an *inert* gas. It neither burns nor supports combustion. By the use of a suitable catalyst nitrogen may be made to combine with hydrogen to form ammonia, NH_3 . (See Haber Process, section 166.) When an electric spark is passed through a mixture of oxygen and nitrogen, nitric oxid, NO , a compound of oxygen and nitrogen is formed. Some of this gas is formed by the lightning during electrical storms. The process is also used commercially in Norway. (See Birkeland-Eyde process, section 171.) At high temperatures metals like aluminum and magnesium unite with nitrogen to form *nitrids*. Magnesium nitrid, Mg_3N_2 , forms ammonia when it decomposes water. The presence of nitrogen may be determined by introducing heated magnesium. If nitrogen is present the nitrid will be formed and ammonia will be set free when water is added.

While compounds of nitrogen are usually formed with some difficulty, many of them are *unstable* and quite easily decomposed. Nearly all modern explosives are made of nitrogen compounds. They liberate large quantities of gas suddenly, hence their decomposition is very violent. Nitroglycerin, T. N. T., picric acid, and nitro-cellulose (smokeless powders), are examples of nitrogen compounds that explode with great violence.

145. Uses of Nitrogen. Nitrogen in the air is a diluent. It makes combustion less rapid in air than in pure oxygen. It also gives bulk to the air, increasing its buoyant force and its pressure.

Plants need nitrogen to make proteins, or albumin. They

can not use *free* nitrogen from the air, however, but must obtain it from the *nitrogen compounds* in the soil. The nitrogen cycle in nature is a most important one. From the soil plants secure nitrogen compounds, water, and mineral matter, and with the carbon dioxide obtained from the air, they make proteins, or plant albumin. As decay occurs ammonia, nitrites, and nitrates are formed and restored to the soil to be used for subsequent nutrition of plants. See Fig. 78.

Very often this natural cycle is interfered with, the plants being used for animal food and transported long distances; thus the nitrogen is removed from the soil and not returned by decay. The soil becomes impoverished and new crops can not be grown

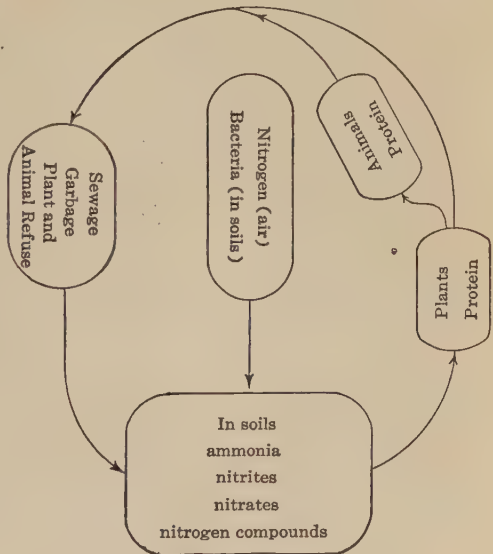


FIG. 78.—Nitrogen cycle.

unless some artificial fertilizer is used to take the place of the natural fertilizing process. The following are some of the most important methods used by farmers for putting nitrogen back into soils that have lost their fertility:

1. *Refuse.* All plant and animal compounds contain nitrogen compounds upon which plants can feed. Ground bone, offal and scrap from slaughter houses, refuse from fish

canneries, garbage, sewage, guano, and barnyard manures are common materials used as fertilizers.

Both garbage and sewage are often wasted, and in many cities large sums of money are paid for the disposal of these products. In some cities both are dumped into rivers, lakes, or the ocean. Garbage is often incinerated. Some progres-

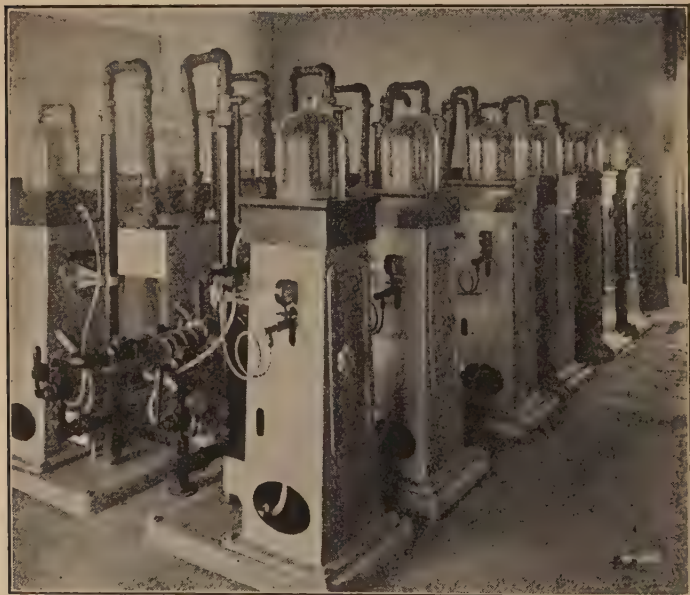


FIG. 79.—Chlorin cylinders for sewage purification.

sive cities have garbage reduction plants. Fats and grease are recovered from the garbage by treatment with steam or a petroleum solvent and used for making soap. The solvent is recovered and used over and over again. The nitrogen-bearing residues which are insoluble are dried and sold to fertilizer manufacturers under the name of *tankage*. Some cities sterilize their sewage by aëration or the use of chemicals and then sell it for use as a fertilizer. Fig. 79 shows cylinders

of chlorin that are being used to purify sewage by destroying bacteria.

2. *Crop Rotation.* We have seen that the continued planting of a single crop that is removed from the farm year after



(J. Russell Smith, *Commerce and Industry*, by permission.)

FIG. 80.—Nodules containing bacteria that take nitrogen from the air.

year leaves the soil impoverished. There are certain crops, however, that the farmer can grow which put nitrogen compounds into the soil. Peas, alfalfa, beans, and clover all have small *nodules* on their roots. See Fig. 80. Bacteria that are

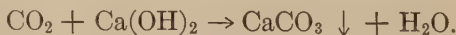
friends to man grow in these nodules. These bacteria in an alkaline soil can take *free* nitrogen from the air and convert it into compounds that plants can use. For breathing we must have *free* oxygen and we would die in water which is 88% oxygen, but in combination. Plants live in air that is 78% free nitrogen, but they can not take it from the air; they are wholly dependent upon nitrogen *compounds* which can be taken in through the roots when dissolved in the soil water. By planting a crop of clover, cow peas, or soy beans every four or five years, the farmer has a fodder crop and at the same time he is putting nitrogen into his soil through the friendly aid of these bacteria. Some Experiment Stations grow these bacteria for inoculating the seeds before they are put into the ground.

3. *Nitrate Beds.* In South America, principally in Chile, extensive beds of sodium nitrate have been discovered in the desert regions. These beds have for a number of years been an important source of sodium nitrate for use as a fertilizer or for making explosives.

4. *Nitrogen Compounds Made Artificially.* Taking free nitrogen from the air and converting it into compounds is commonly known as *nitrogen fixation*, or *nitrification*. Several processes are now in use. The Birkeland-Eyde process (see page 197), the Haber process (see page 187), and the *cyanamid* process (see page 188) are commercial processes of *fixing nitrogen* that are discussed in later chapters.

C. CARBON DIOXID AND WATER VAPOR

146. Carbon Dioxid. When carbon dioxid comes into contact with limewater, it produces a milky white precipitate of calcium carbonate.



This serves as a test for carbon dioxid gas. When a bottle containing limewater is exposed to the air a crust of calcium

carbonate forms on its surface, showing that the air contains carbon dioxid. The amount present in out-door air varies slightly. Several factors tend to increase the percentage: 1. Our chimneys belch out into the air millions of tons of carbon dioxid annually. In fact every ton of carbon burned gives off $3\frac{2}{3}$ tons of carbon dioxid. 2. Every animal takes oxygen from the air and exhales carbon dioxid. Part of the carbon in our food is oxidized to carbon dioxid. 3. In the process of decay some carbon dioxid is formed and finds its way into the air.

There are at least two important ways in which the amount of carbon dioxid present in the air is being decreased: 1. All

plants that have green coloring matter in their tissues take carbon dioxid in through their leaves. Using the energy from sunlight, they split up the carbon dioxid, keep the carbon for use in making starch, and give out the oxygen

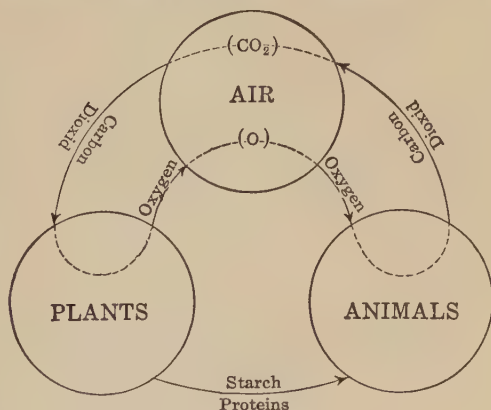


FIG. 81.—Carbon dioxid cycle.

again to the air. 2. As the solid rock of the earth's crust disintegrates, or weathers, carbon dioxid in water solution unites with certain substances forming carbonates. The student needs to bear in mind the fact that carbon dioxid unites chemically with water to form a weak acid known as carbonic acid, H_2CO_3 . Just how closely plants and animals are related is shown in Fig. 81. Animals and plants are mutually dependent, since plants supply oxygen for animals and the

animals in turn exhale the carbon dioxid without which plants could not prepare their food. We may summarize the so-called *oxygen-carbon dioxid cycle* in the following brief statement: *Animals inhale oxygen and exhale carbon dioxid; plants absorb carbon dioxid during photosynthesis and give out oxygen.*

147. Water Vapor in the Air. Deliquescent substances become wet when exposed to the air. A glass of ice water standing in a warm room soon becomes covered with drops of water. These tests, as well as the fact that rain falls occasionally, show that the air contains water vapor.

The amount of water vapor the air can hold is its capacity. It is usually expressed in grains per cubic foot. The capacity increases as the temperature rises. The amount of water vapor the air does hold at a given time is called its absolute humidity. Absolute humidity is expressed in grains per cubic foot. The absolute humidity of outdoor air depends upon several factors, but chiefly upon proximity to a large body of water from which evaporation may occur. The relative humidity equals $\frac{\text{absolute humidity}}{\text{capacity}}$.

Raising the temperature *decreases* the relative humidity and the air feels drier since the capacity is increased by a rise in temperature. Lowering the temperature lowers the capacity and *increases* the relative humidity, making the air feel damp. When the relative humidity becomes 100%, the *dew-point* is reached. A further cooling of the air then results in precipitation of some of the moisture as rain, snow, etc.

A high relative humidity makes the heat oppressive in summer and the cold seem more severe in winter. We say the air is "heavy." In reality it is "light," since 1 liter of water vapor at standard temperature and pressure weighs only 0.81 gram. When the relative humidity is too low, the perspiration evaporates rapidly and the skin feels dry; when the relative humidity is very high, the perspiration

does not evaporate and the skin is clammy and sticky. We are most comfortable when the relative humidity is from 40 to 60%.

148. Ventilation. Since we exhale carbon dioxid and inhale oxygen the air in a closed room will soon show a higher percentage of carbon dioxid than 4 parts in 10,000. Unless some method of exchanging this exhaled air for pure air is used, it soon becomes foul not only because there is a decided increase in the per cent of carbon dioxid present, but organic impurities given off from the lungs make it still more impure. The relative humidity is increased at the same time, thereby increasing the discomfort. *Ventilation consists in exchanging the foul air of a room or building for pure air drawn from out of doors.* The principle of ventilation depends upon the fact that warm air is lighter than cold air. In window ventilation an opening near the top of the room furnishes an exit for the impure air as colder, pure air enters through an opening nearer the floor. In many large buildings pure air is forced into the room by motor-driven fans. The New Jersey State law requires that 1800 cu. ft. of fresh air be supplied per hour for each pupil in a schoolroom. Experiments have shown that much of the discomfort in crowded halls is due to the increased relative humidity. In the winter time furnace-heated buildings are quite likely to have too low a relative humidity and we hear a good deal about "schoolroom deserts." Many large buildings have humidifiers which wash the air to free it from dust and supply enough moisture to keep the relative humidity near the desired percentage. Some department stores have hygrometers scattered about the different floors and it is the duty of an employee to take readings of the relative humidity at intervals.

D. ARGON AND THE RARE GASES

149. Argon. In 1894 argon was discovered by Sir William Ramsay and Lord Rayleigh. They observed that nitrogen

prepared by the first method given in section 143 is somewhat heavier than the *pure* nitrogen obtained by using the second method. By a tedious process they continued to remove oxygen and nitrogen from air until a rather heavy, inactive gas was left. The name *Argon* is given to this lazy gas. Argon is now prepared from liquid air. The nitrogen and argon boil off first. The nitrogen is then removed by

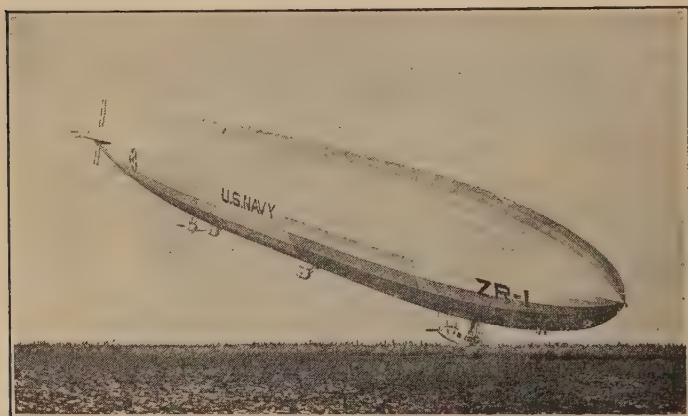


FIG. 82.—The ZR-1, or Shenandoah, is 680 ft. long, 96 ft. wide, and 78 ft. in diameter. The frame is made of duralumin, an alloy of copper, manganese, and aluminum. The 20 gas bags have a capacity of 2,100,000 cu. ft. Six 300 H. P. engines are used to drive the Shenandoah, which weighs 75,000 lb.

passing these two gases over calcium carbide heated to a temperature of 800°C .

Argon is colorless, odorless, and tasteless. It is slightly heavier than air. It seems to be absolutely inert or inactive. No compounds of argon are known. Argon finds use in filling the bulbs of tungsten rectifiers. Some of the gas-filled electric light bulbs contain about 80% argon and 20% nitrogen. The tungsten does not evaporate so rapidly in a gas-filled bulb, and the bulb does not darken so quickly.

150. Helium. Helium was first discovered in the sun's atmosphere by Sir Norman Lockyer in 1868, but it was 27 years before Ramsay isolated it from the other constituents of the air. Helium is one of the lightest gases known, being only twice as heavy as hydrogen. Helium is inactive, no compounds of the element being known.

Since helium is not inflammable it is used in military balloons. Fig. 82 shows the Shenandoah built by the U. S. Navy. Its gas bags contain helium. Its buoyancy is nearly 93% as great as hydrogen, but it can not be enkindled by .



FIG. 83.—Compressor used at Fort Worth, Texas, for liquefying helium.

incendiary bullets or from the engines in the case of dirigibles. Prior to the World War helium sold for about \$1700 per quart. When its importance for military purposes was realized, search for a more abundant supply was begun. Helium forms about 2% of the natural gas from wells in Kansas, Texas, and Oklahoma. The helium is separated from the other gases by cooling and compressing them in liquid air machines until everything liquefies but the helium, which may then be separated from the liquid. See Fig. 83. By this process the cost of producing helium is about 10¢ per quart. Liquid helium boils at the very low temperature of -268.5°C . By evaporating liquid helium Kamerlingh

Onnes recently succeeded in getting a temperature within less than one degree of absolute zero.

151. Rare Gases. *Neon* (new), *krypton* (hidden), and *xenon* (stranger) are three gases rather recently discovered in our atmosphere. All are inert, forming no compounds. No use is known for the latter two, but *neon* finds some use in spark plug testers and in neon lamps. When a tube containing neon is held against a spark plug, it will be filled with a reddish-orange light provided the coil is giving high enough voltage and the plug is sparking properly. The neon lamp is used in some cities for advertising signs, since the current consumption is very small. Neon is sometimes used with the mercury vapor lamp to supply the red rays in which this lamp is deficient.

SUMMARY

Air has weight and exerts pressure. Its chief constituents are *oxygen*, *nitrogen*, *carbon dioxid*, and *water vapor*.

Nitrogen may be obtained from the air by removing the oxygen with some chemical, such as phosphorus. Pure nitrogen is prepared by heating a mixture of *ammonium chlorid* and *sodium nitrite*.

Nitrogen is odorless, colorless, tasteless; it is non-poisonous. Nitrogen is slightly soluble in water and a little lighter than air.

Nitrogen neither burns nor supports combustion; it is quite inert. Under certain conditions it unites with oxygen, hydrogen, and a few metals.

Nitrogen compounds are needed by plants to form proteins. The *nitrogen cycle* in nature is a very important one, since plants make food for themselves and for animals.

Plants take in carbon dioxid and set free oxygen; animals inhale oxygen and exhale carbon dioxid. Thus animals and plants are mutually dependent.

The ratio of the amount of water vapor the air does hold to what it could hold if saturated is its *relative humidity*. It is always expressed in per cent.

Argon, neon, xenon, krypton, and helium are all inert gases found in the air. They form no known compounds.

Gases may be liquefied by compressing them and then letting

them expand. All gases have been liquefied, helium at a temperature within 5° of absolute zero.

QUESTIONS

1. What changes would take place if the air were pure oxygen or the percentage of oxygen were increased?

2. Discuss the importance of nitrification, or nitrogen fixation.

3. Why are traces of nitrogen compounds found in the air after a thunderstorm?

4. How could you obtain air free from carbon dioxide? Free from water vapor?

5. How would you take the oxygen out of ordinary air? The nitrogen?

6. Why do the constituents of the air vary so little in their relative amounts?

7. Liquid air becomes blue when it stands for some time. Explain.

8. Why does liquid air boil so vigorously when poured into a vessel standing on a cake of ice?

9. Would it be a good idea to stopper a thermos bottle or a Dewar flask containing liquid air? Explain.

10. Can it ever rain while the air is being warmed? Would expansion or compression of the air be more likely to produce rain?

CHAPTER XVI

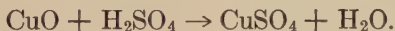
ACIDS, BASES, AND SALTS

152. Acids, Bases, and Salts. Of the many compounds studied in chemistry, a large number belong to one of the three following classes: *acids, bases, and salts*. In the laboratory we have already used hydrochloric and sulfuric acids. We are familiar with the base sodium hydroxid from our study of the effects of sodium on water. The salt sodium chlorid is typical of a large number of compounds known as *salts*. In this chapter the general characteristics of each of these three classes will be studied, exemplified by some of the most common representatives.

A. ACIDS

153. Acids. At the ordinary temperature some acids are gaseous, some are liquid, and others solid. For example, hydrogen chlorid and hydrogen sulfid are gases; nitric acid and sulfuric acid are liquids; tartaric, boric, and oxalic acids are solids. While acids have no physical properties in common, yet in water solution they have many chemical properties that are characteristic. Since the *pure* acid does not have these *acid properties*, the name acid usually refers to a *solution of the acid in water*. For example, concentrated nitric acid (HNO_3) is a water solution, 68% nitric acid to 32% of water. The *dilute* nitric acid as used in the laboratory is made by mixing one part of this acid with four or five parts of water, probably about 12% acid. Ordinary sulfuric acid is about 93.5% acid to 6.5% water. The dilute acid is made by adding one part of the acid by volume to six parts of water.

154. General Characteristics of Acids. Certain characteristics are common to all acids: (1) *They contain hydrogen*; Lavoisier thought that all acids contain oxygen. Most of them do, but it is not essential as in the case of hydrogen. (2) *They have a sour taste*. The taste of unripe fruits, lemon, and grape fruit is due to the acid they contain. (3) *They change the color of certain substances known as indicators; thus acids change the color of litmus from blue to red*. (4) *They neutralize bases forming salts and water*. The acid loses its characteristic properties and at the same time the base is destroyed. (5) *Acids act on certain metals forming salts and liberating hydrogen*. Recall the preparation of hydrogen, section 39. (6) *Acids interact with the oxids of metals forming salts and water*. For example,



155. Preparation of Acids. When we studied the chemical properties of water we found that it unites readily with the oxids of non-metals to form acids. For example, SO_3 , the oxid of the non-metal sulfur, unites with water to form sulfuric acid, H_2SO_4 .



The oxid of a non-metal that unites with water to form an acid is called an acid anhydrid. The above equation is reversible. When sulfuric acid is rendered anhydrous by removing the water, the *acid anhydrid* remains. Nitrogen pentoxid, N_2O_5 , is the anhydrid of nitric acid as the following equation shows:



Most acids are not made by adding water to their anhydrids, but by an entirely different method of preparation. Suppose we desire to prepare nitric acid, HNO_3 ; it contains

hydrogen and the NO_3 radical. Sodium nitrate, a compound found extensively in Chile, contains the same radical. By heating this compound with sulfuric acid metathesis occurs:



The NO_3 radical combines with half the hydrogen of the sulfuric acid to form nitric acid. The negative HSO_4 radical combines with the sodium. Hydrogen chlorid is prepared in an analogous manner by the action of sulfuric acid on sodium chlorid.



The gas that is driven off is dissolved in pure water and sold under the name of *hydrochloric acid*.

Most acids are prepared by heating a salt of the acid we wish to prepare with sulfuric acid. For three reasons we use sulfuric acid in preparing other acids: (1) *It is the cheapest acid.* (2) *Its boiling point is higher than that of most other acids.* (3) *It is fairly stable.* If sulfuric acid vaporized or decomposed at a lower temperature than that needed to vaporize other acids, the product that distils over would be contaminated with sulfuric acid itself or with its decomposition products.

156. Naming of Acids. Acids that are made up of two elements only are named as other binary compounds. HCl is hydrogen chlorid; unfortunately its water solution is called hydrochloric acid. The beginner in chemistry is sometimes confused because of this irregularity. Other examples of acids that contain two elements only are hydrogen bromid, HBr , and hydrogen sulfid, H_2S .

We have learned that all acids contain hydrogen. Nearly all acids also contain oxygen. The method of naming acids that contain oxygen is not so simple since the same acid forming element often forms a series of acids. For example,

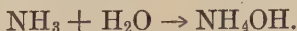
the following oxygen acids of chlorin are known: HClO_4 , HClO_3 , HClO_2 , and HClO . Since they all contain chlorin the root "*chlor*" is used in all cases. The most common of the oxygen acids takes the ending *ic*. For example, HClO_3 , the most common *oxygen* acid of chlorin, is called *chlor-ic* acid. The acid containing less oxygen than the *ic* acid takes the ending *ous*. Thus *chlor-ous* acid is HClO_2 . The same ending is used for the acid containing still less oxygen than the *ous* acid, but the Greek prefix *hypo* (under) is used. HClO is the formula for *hypo-chlor-ous* acid. The acid containing more oxygen than the *ic* acid takes the ending *ic*, but the Latin prefix *per* (thoroughly saturated with) is used. The formula for *per-chlor-ic* acid is HClO_4 . For comparison the following acids are given with their formulas:

Acids	Formulas	Acids	Formulas	Acids	Formulas
<i>per-sulfuric</i>	$\text{H}_2\text{S}_2\text{O}_8$	—	—	—	—
<i>sulfuric</i>	H_2SO_4	<i>nitric</i>	HNO_3	<i>bromic</i>	HBrO_3
<i>sulfurous</i>	H_2SO_3	<i>nitrous</i>	HNO_2	—	—
<i>hypo-sulfurous</i>	$\text{H}_2\text{S}_2\text{O}_4$	<i>hypo-nitrous</i>	$\text{H}_2\text{N}_2\text{O}_2$	<i>hypo-bromous</i>	HBrO

The student will observe some irregularities and some omissions. In some cases the full series of acids is not known.

B. BASES

157. Bases. The following bases are the most common: sodium hydroxid, potassium hydroxid, ammonium hydroxid (aqua ammonia), and calcium hydroxid. *Sodium hydroxid* and *potassium hydroxid* are white deliquescent solids, very soluble in water. *Ammonium hydroxid* is a compound formed by dissolving ammonia gas in water.

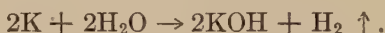
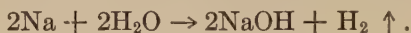


Calcium hydroxid is slightly soluble in water. Its water solution is known as *limewater*. The soluble bases that have

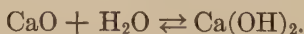
the characteristics of strong bases given in the following paragraph are called *alkalis*.

158. Characteristics of Soluble Bases. (1) *Bases contain a metal and one or more hydroxyl (OH) groups.* (2) *They have a bitter taste.* (3) *Bases affect indicators; they turn red litmus blue and change a solution of phenol-phthalein from colorless to red.* (4) *Bases neutralize acids forming salts and water.* (5) *They have a slippery feeling when in solution.* (6) *The strong bases act corrosively on the flesh, especially attacking fats and converting them into soaps.*

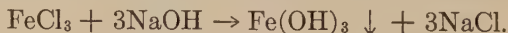
159. Preparation of Bases. 1. Such active metals as sodium and potassium interact with water to form bases; hydrogen gas is liberated. Calcium acts on water slowly forming calcium hydroxid, a base. The equations are as follows:



2. The oxids of some metals unite with water to form bases. *The oxid of a metal that unites with water to form a base is called a basic anhydrid.* The following reversible equation shows the action between calcium oxid, a basic anhydrid, and water.



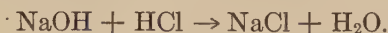
Insoluble bases are prepared by adding to the solution of a compound containing the metal some soluble base. Metathesis occurs, the insoluble base being precipitated. In the following equation the insoluble base is ferric hydroxid.



160. Nomenclature of Bases. The method of naming bases is extremely simple. They take the name of the metal

from which they are formed followed by the word *hydroxid*. Formerly they were called hydrates and the name is still used occasionally. Because they act so readily on the skin and flesh, sodium hydroxid and potassium hydroxid are often called *caustic soda* and *caustic potash* respectively.

161. Neutralization. If we add 1 mole of sodium hydroxid in solution to 1 mole of hydrochloric acid, *neutralization* occurs as represented by the following equation:



The solution that is formed affects neither blue nor red litmus. It does not have any of the characteristic properties of either the base or the acid. We say the solution is *neutral*. If we evaporate the solution, water is driven off and sodium chlorid, a *salt*, remains as a crystalline solid. *Neutralization is the name given to the process that occurs when an acid and a base are brought together in such proportions that each destroys the properties of the other. A salt and water are the products formed.*

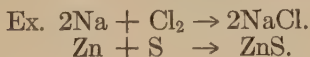
C. SALTS

162. Salts. The properties of salts are so widely divergent that it is almost impossible to give any general properties. They are usually crystalline solids. Their color varies; the majority are white, but cobalt salts are pink, copper salts are blue, and nickel and ferrous iron salts are green. Most salts are to a greater or lesser degree soluble in water. Nitrates are all soluble. Chlorids and sulfates are generally soluble.

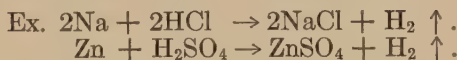
163. Preparation of Salts. There are several ways of preparing salts. We have already learned that a salt is formed: (1) when a metal interacts with an acid; (2) when the oxid of a metal interacts with an acid; (3) when an acid neutralizes a base. There are also other methods of preparing

salts. Quite often the same salt may be prepared by several different methods. The following equations are examples of the various methods:

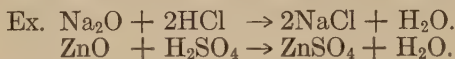
(1) *By the Direct Union of the Elements.*



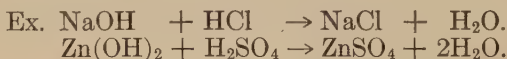
(2) *Interaction of Acid and Metal.*



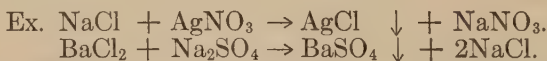
(3) *The Action of an Acid on the Oxid of a Metal.*



(4) *Neutralization.*



(5) *Metathesis.*



This last method of preparing salts is a very useful one. We begin with two salts and prepare two different salts. When we mix solutions of sodium chlorid and silver nitrate, as shown in the first equation, *insoluble* silver chlorid comes down as a precipitate. The sodium nitrate which is formed at the same time remains in solution. It may be recovered by evaporating the excess water. In the second equation insoluble barium sulfate is precipitated. This method will apply only when one of the salts is insoluble or if one product is volatile.

164. Naming of Salts. Since a salt is really composed of the metal of a base and an acid-forming element, or an

acid radical, it is named from both base and acid. Salts take the name of the metal of the base from which they were formed, use the root and prefix of the acid, but change the ending *ic* to *ate* and the ending *ous* to *ite*. The following table illustrates the method of naming the salts that are formed when sodium hydroxid neutralizes the chlorin acids discussed in section 156:

ACIDS		SALTS	
HClO ₄	per-chlor- <i>ic</i>	NaClO ₄	sodium per-chlor- <i>ate</i>
HClO ₃	chlor- <i>ic</i>	NaClO ₃	sodium chlor- <i>ate</i>
HClO ₂	chlor- <i>ous</i>	NaClO ₂	sodium chlor- <i>ite</i>
HClO	hypo-chlor- <i>ous</i>	NaClO	sodium hypo-chlor- <i>ite</i>
HCl	hydrogen chlorid, or hydrochloric	NaCl	sodium chlor- <i>id</i> .

SUMMARY

All acids contain hydrogen; they have a sour taste, turn blue litmus red, act on metals forming a salt and hydrogen, act on oxids of metals forming a salt and water, and neutralize bases.

The oxid of a non-metal that unites with water to form an acid is called an *acid anhydrid*. Acids are generally prepared by the action of sulfuric acid on a salt that contains the acid-forming element or group of elements.

The most common acid containing oxygen has the ending *ic*. An acid in the same series containing less oxygen has the ending *ous*. When an acid has still less oxygen than the *ous* acid in the series, it takes the ending *ous*, but uses the prefix *hypo*. An acid having more oxygen than the *ic* acid takes the *ic* ending and uses the prefix *per*.

Bases contain one or more *hydroxyl* groups; they have a bitter taste, turn red litmus blue, and neutralize acids. Soluble bases have a slippery feeling and readily saponify fats to form soaps.

Bases are prepared by the action of a metal or the oxid of a metal on water.

When a base is added to an acid the properties of both are destroyed. The process is called *neutralization*. Water and a salt are formed.

Salts may be prepared in several ways: (1) *synthesis*; (2) *neutralization*; (3) *action of an acid on a metal*; (4) *action of an acid on the oxid of a metal*; (5) *double decomposition*.

Salts take the name of the metal of the base from which they are formed, use the same root and prefix as the acid, and change the acid ending *ic* to *ate*; the ending *ous* to *ite*.

QUESTIONS

1. Of what acid is CO_2 the anhydrid? SO_2 ? N_2O_3 ? P_2O_5 ?
2. From the rules for naming salts what ending would you expect a salt formed from hydrochloric acid to have? What is the correct ending? Why?
3. Name as many foods as you can that contain acids. How would you verify your conclusion?
4. If sodium hydroxid and potassium hydroxid were the same price per pound which would you use as a base? Explain.
5. Which one of the bases mentioned in section 157 would you use to clean a greasy sink? To remove grease spots from clothing? To neutralize acid stains on clothing?
6. How many moles of sodium hydroxid are needed to neutralize one mole of hydrochloric acid? One mole of sulfuric acid? One mole of phosphoric acid?
7. What products are formed when iron and hydrochloric acid interact? By the interaction of iron and sulfuric acid?
8. What products are formed when hydrochloric acid acts on ferrous oxid, FeO ? When sulfuric acid acts on zinc oxid, ZnO ?

EQUATIONS AND PROBLEMS

1. Phosphoric acid has the formula H_3PO_4 . Write the formula for phosphorous acid. For hypo-phosphorous acid.
2. The following acids have the ending *ic*: HIO_3 ; HBrO_3 . Write the formulas and names for as many other acids in the series as possible.
3. Balance and complete the following neutralization equations: (Remember that the products of such reactions are water and a salt).

(a) $\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow$	(d) $\text{Ca(OH)}_2 + \text{HCl} \rightarrow$
(b) $\text{NaOH} + \text{H}_3\text{PO}_4 \rightarrow$	(e) $\text{Ca(OH)}_2 + \text{H}_3\text{PO}_4 \rightarrow$
(c) $\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow$	(f) $\text{Al(OH)}_3 + \text{H}_2\text{SO}_4 \rightarrow$
4. Balance and complete the following:

(a) $\text{Al} + \text{H}_2\text{SO}_4 \rightarrow$	(d) $\text{CaO} + \text{HCl} \rightarrow$
(b) $\text{Na} + \text{H}_2\text{SO}_4 \rightarrow$	(e) $\text{MgO} + \text{H}_2\text{SO}_4 \rightarrow$
(c) $\text{Ca} + \text{HCl} \rightarrow$	(f) $\text{Na}_2\text{O} + \text{H}_3\text{PO}_4 \rightarrow$

5. Give the correct names of all the salts formed in the equations of problems 3 and 4.

6. Devise three methods of forming the salt potassium chlorid, KCl. Three methods of preparing calcium nitrate, $\text{Ca}(\text{NO}_3)_2$.

7. How many grams of sodium hydroxid will be required to neutralize 85 gm. of hydrogen chlorid?

8. How many pounds of sulfuric acid will be needed to prepare 200 lb. of nitric acid? (See equation on page 178).

9. How many pounds of sodium nitrate will be needed to prepare 200 lb. of nitric acid?

CHAPTER XVII

AMMONIA AND AMMONIUM COMPOUNDS

165. Introductory. A solution of ammonia gas in water is known as *household ammonia*. It is the pungent gas that arises from such a solution that is known to chemists as *ammonia*. It has the formula NH_3 . Traces of ammonia are found in the air, since this gas is formed by the decay of plant and animal matter. As it dissolves in the rain water it finds its way into the soil, where it is also formed by decay of organic matter in the presence of bacteria that cause putrefaction. The odor of ammonia may be noticed in the vicinity of stables where farm animals are housed.

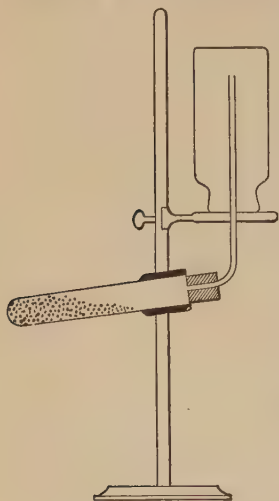
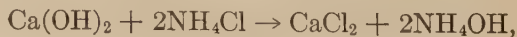


FIG. 84.—Apparatus for preparing ammonia.

166. Preparation. 1. *Laboratory.* Ammonia is prepared in the laboratory by heating a mixture of slaked lime (calcium hydroxid) and ammonium chlorid. The gas is collected by air displacement. See Fig. 84. In the equation,

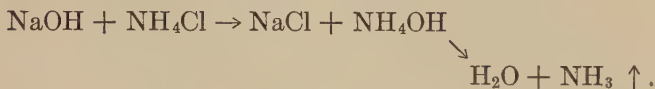


the NH_4 group acts as a *positive* radical and takes the place of calcium by substitution. Since the compound

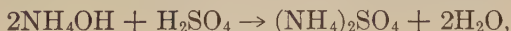
NH_4OH is unstable, the heat of the reaction breaks it up into ammonia, NH_3 , and water.



Any strong base may be used instead of calcium hydroxid in the preparation of ammonia, and any ammonium salt may be substituted for ammonium chlorid. In the following equation sodium hydroxid is used:

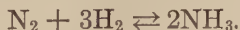


2. *Commercial.* (a) *From Coal.* At one time ammonia was prepared by distilling hoofs and horns, hence the old name "spirits of hartshorn." Now one of the important commercial sources of ammonia is soft coal. When coal is heated in retorts to prepare illuminating gas, ammonia is given off as a by-product. The ammonia dissolves in the water used to wash the gas, and the solution is neutralized with sulfuric or hydrochloric acid. When sulfuric acid is used,



ammonium sulfate is formed. This salt is then decomposed with slaked lime and the ammonia is dissolved in pure water. (See equation under laboratory preparation.) Such a solution forms the *aqua ammonia* of commerce.

(b) *Haber Process.* It seems as if we ought to be able to form ammonia by combining one volume of nitrogen with three volumes of hydrogen as follows:



When an electric spark is passed through such a mixture, *only* about 2% of the gases combines, because the reaction is

reversible. Haber, a German chemist, found a method of increasing this yield to about 8%. The gases under a pressure of about 200 atmospheres are passed through a tube containing a suitable catalyst, such as finely divided iron or uranium carbid. The temperature is kept at about 500 or 600° C. The ammonia is absorbed in water and the uncombined gases are then led through the apparatus again.



FIG. 85.—Fractionating columns at the Muscle Shoals plant.

Thus the process is continuous since new gases are added. Large plants were constructed in Germany to make ammonia by this process before the beginning of the World War. (See section 144.)

(c) *Cyanamid Process.* Several plants were constructed by the United States Government to make nitrogen compounds for military purposes during the World War. One of these plants, at Muscle Shoals, Alabama, is still intact. This plant was making nitrogen compounds from the air when the armistice was signed.

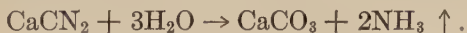
Nitrogen obtained from liquid air by fractional distillation

is passed over calcium carbid at a temperature of about 800°C . Fig. 85 shows the fractionating columns in which the nitrogen is separated from the other constituents of the air. The nitrogen combines with the carbid to form calcium cyanamid, CaCN_2 . Superheated steam converts this com-



FIG. 86.—In these autoclaves ammonia is formed from calcium cyanamid.

pound into ammonia as represented by the following equation:



Huge autoclaves in which the ammonia is formed by the action of the superheated steam are shown in Fig. 86. By a process discussed in a later chapter, section 171, the ammonia may be converted into nitric acid for use in making explosives. Both the Haber and the cyanamid processes are commercial methods of *fixing* nitrogen. In time of peace the plant at Muscle Shoals can be used

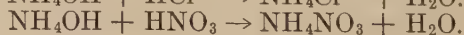
to manufacture fertilizers. It has potential value as an arsenal in case of war.

167. Physical Properties of Ammonia. Ammonia is a gaseous compound having the formula NH_3 . It has a peculiar, pungent odor and a bitter taste. Ammonia is lighter than air and very soluble in water. One liter of water at 20°C . dissolves 710 liters of ammonia gas. At 0°C . one liter of water dissolves almost 1300 liters of the gas. The very high solubility is probably due to a chemical union between the gas and water to form ammonium hydroxid.

The ammonia water thus formed is lighter than water, the specific weight of the 35% solution being 0.88. When ammonia water is boiled the gas is all driven off. Even under ordinary atmospheric pressure ammonia gas condenses to a liquid when sufficiently cooled. Its boiling point is -34°C . Liquid ammonia is put on the market compressed in steel cylinders.

168. Chemical Properties. Ammonia neither burns nor supports combustion. In oxygen, however, it burns slowly. Heated with copper oxid, it forms water and nitrogen. The water solution of the gas contains a compound having the formula NH_4OH .

The NH_4 group acts as a radical. It combines with the OH radical in water solution, and the compound NH_4OH acts like a base. In this case the NH_4 radical acts just as the active metals, sodium and potassium, do with the OH radical. Students must never confuse the *ammonium radical*, NH_4 , with the compound *ammonia*, NH_3 . While ammonium acts like a metal in compounds, yet it can not be isolated as NH_4 . It always breaks up into ammonia and hydrogen when it is separated from the negative element or radical with which it was combined. The following equations show the behavior of the ammonium radical, NH_4 .



169. Uses of Ammonia. 1. *As a Fertilizer.* The importance of ammonia and ammonium compounds as fertilizers was discussed under nitrogen.

2. *As a Detergent.* Since aqua ammonia is a base we would expect it to act upon fats and oils. It is quite extensively used in the household for removing grease spots. Since the gas is liberated as soon as the water evaporates, it does not injure the fabric as do such bases as sodium and potassium hydroxid. It may dissolve the dye in a colored fabric, however.

3. *For Refrigeration.* If we pour water on one hand and let it evaporate quickly, the hand is cooled. It requires heat to convert water into its vapor. In this illustration, the heat came from the hand, thus producing the cooling effect. If we use alcohol instead of water the cooling effect is more marked, since alcohol evaporates more rapidly. Since alcohol, boiling at 78°C. , produces a more marked cooling effect than water, boiling at 100°C. , we would expect liquid ammonia, which boils at -34°C. , to take in heat very rapidly as it evaporates. This *principle of cooling by evaporation* is used in making ice. The liquid ammonia as it evaporates takes so much heat away from the water that the water freezes. It requires about 295 calories of heat to convert one gram of liquid ammonia into gaseous ammonia. If we take 80 calories away from one gram of ice water, the water freezes. The heat used to evaporate the liquid ammonia is constantly taken from the surrounding water until it is finally converted into ice.

Fig. 87 shows how the principle is applied. By using a compression pump *P*, ammonia gas is liquefied in the pipes, *C*, around which cold water flows to absorb the heat liberated as the gas liquefies. The liquid ammonia passes through an expansion valve, *V*, into a series of coils, which are immersed in the brine tank *E*. As the ammonia in the coils evaporates, heat is absorbed until the brine is

cooled below the freezing point of fresh water. Cans of fresh water immersed in the brine are frozen after several hours into cakes of solid ice.

In cold storage plants the cold brine is pumped through pipes in the storage room. Just as hot water flowing through

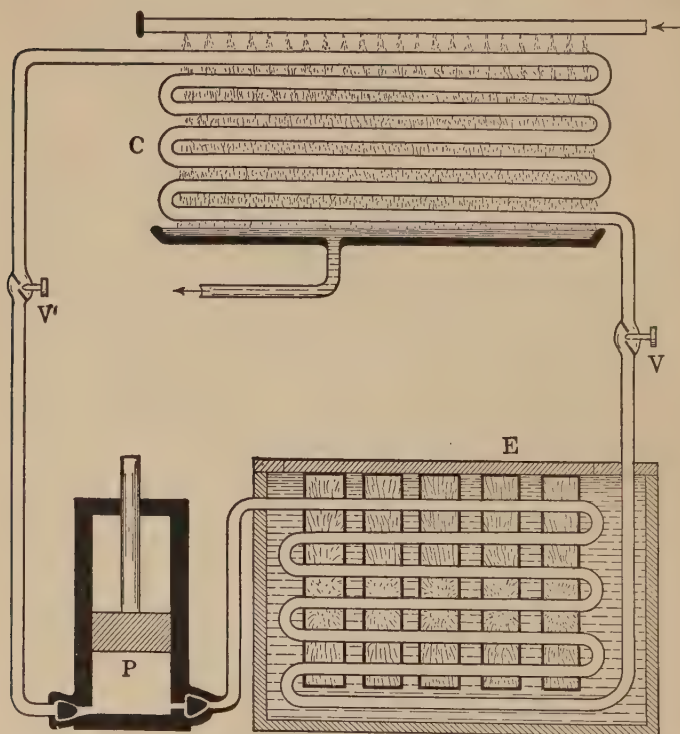


FIG. 87.—Diagram to illustrate the manufacture of ice.

pipes in a room warms it by radiation, so the circulation of cold brine cools the room and keeps it at any desired temperature.

SUMMARY

Ammonia is formed by the decay of animal and vegetable matter. It is prepared in the laboratory by heating a mixture of *calcium hydroxid* and *ammonium chlorid*. Commercially ammonia is obtained as a by-product from the distillation of soft coal. Ammonia is prepared from the elements by passing a mixture of nitrogen and hydrogen over a suitable catalyst to facilitate combination. At Muscle Shoals ammonia is made by treating calcium cyanamid with superheated steam.

Ammonia is a colorless gas; it may be identified by its peculiar odor; it is very soluble in water.

Ammonia neither burns nor supports combustion. Its water solution is a base called *ammonium hydroxid*. In this base the NH_4 radical acts like a metal.

Ammonia finds use as (1) a *fertilizer*; (2) a *detergent*; and (3) in *refrigeration* or the making of artificial ice.

QUESTIONS

1. Dry ammonia gas does not affect litmus paper. Explain.
2. Gases are often dried by bubbling them through concentrated sulfuric acid. Could ammonia be dried in this manner? Explain.
3. Why is ammonia called the volatile alkali?
4. What is meant by the ammonium theory?
5. Why is *brine* used in the tanks containing the cans of fresh water for making ice?
6. Suppose you were given a compound that you suspected contained the ammonium radical. How would you verify your suspicion?
7. Why are the processes of fixing atmospheric nitrogen so important?
8. Write equations to show the interaction of ammonium hydroxid with the following acids: H_2SO_4 ; H_2CO_3 ; H_3PO_4 .

PROBLEMS

1. How many grams of ammonia can be prepared from 40 gm. of ammonium chlorid?
2. How many grams of ammonium chlorid are needed to prepare 20 liters of ammonia?
3. Find the weight of one liter of ammonia. What is the "specific weight" of ammonia gas, air standard? Hydrogen standard?

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4. How many grams of calcium hydroxid are needed to react with 140 gm. of ammonium sulfate?

5. In the Haber process how many liters of hydrogen are required to combine with 500 liters of nitrogen? How many liters of ammonia are formed at standard temperature and pressure? How many liters of water at zero degrees Centigrade will be needed to absorb this ammonia?

CHAPTER XVIII

NITRIC ACID AND THE OXIDS OF NITROGEN

A. NITRIC ACID

170. Introductory. One of the strongest acids known is nitric acid, which has the formula HNO_3 . This acid was well-known to the early alchemists under the name *aqua fortis* (strong water). The acid and its method of preparation were described by Geber, an alchemist who lived in the 8th century.

171. Preparation. (a). *Laboratory.* For preparing nitric acid in the laboratory we make use of the general method outlined in section 155. A

salt of nitric acid is heated in a retort with sulfuric acid. Any nitrate may be used, but sodium nitrate is usually chosen because it is the only nitrate occurring in nature in any considerable quantity. See Fig. 88. The nitric acid volatilizes and its vapor is condensed in the tube of the retort and in the receiver *F*. If an excess of sulfuric acid is used, the reaction is represented by the following equation:

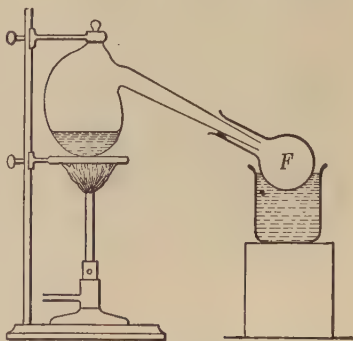


FIG. 88.—Preparation of nitric acid.



This reaction takes place at a fairly low temperature and the unstable nitric acid is not decomposed.

(b) *Commercial Preparation.* (1) *From sodium nitrate.*

One commercial method of preparing nitric acid does not differ essentially from the laboratory method just given. Sodium nitrate, or Chile saltpeter, is heated with sulfuric acid in iron retorts. The nitric acid is condensed in large bottles containing a little water.

(2) *The Arc Process.* At very high temperatures, 3000°C . or more, nitrogen and oxygen combine to form nitric oxid, NO . The yield is relatively small, since the following equation is reversible:

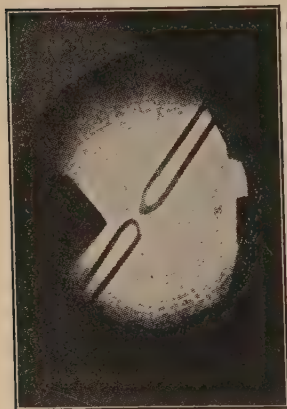
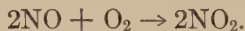


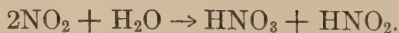
FIG. 89.—Arc several feet in diameter for making nitric oxid.

Large electric plants have been constructed, especially in Norway where electrical power is cheap, for producing a very large electric arc. This arc (see Fig. 89) is spread out into the form of a disc several feet in diameter by means of electro-magnets. Moist air is then blown through the arc to form nitric oxid. The nitric oxid

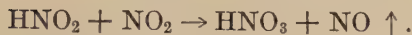
takes more oxygen from the air forming nitrogen *peroxid*, NO_2 , as shown in the equation,



At ordinary temperature this reddish-brown gas dissolves in water forming nitric acid and nitrous acid.



At a slightly higher temperature the nitrous acid is oxidized to nitric acid by the further action of more NO_2 .



The nitric oxide that is left combines readily with more oxygen and may be used again for further oxidation. Fig. 90 shows the furnaces in which the oxidation occurs. This process is known as the Birkeland-Eyde process. The nitric

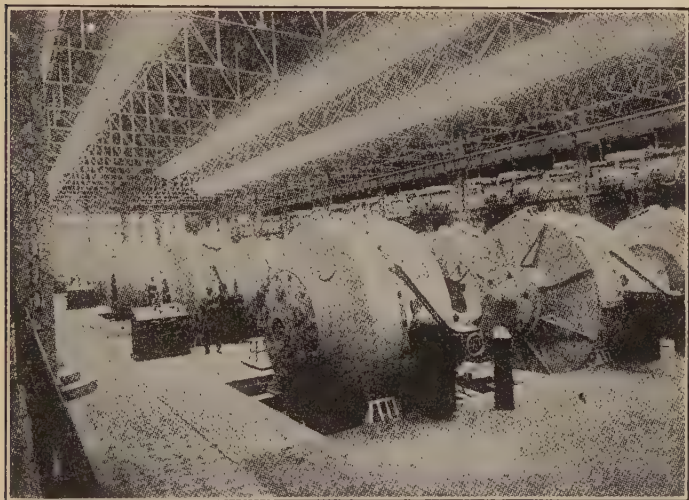


FIG. 90.—Furnaces in which nitric oxide is made by the Birkeland-Eyde process.

acid is generally neutralized with slaked lime and the calcium nitrate is then sold as a fertilizer.

(3) *From Ammonia.* We know that it is possible to oxidize ammonia and form nitric acid. The equation for the reaction follows:



Ammonia, which may be made either by the Haber or the cyanamid process, is mixed with air and passed through platinum gauze as a catalyst. The gauze is heated electrically to a temperature of about 750°C . This process of making

nitric acid was used quite extensively during the World War. Fig. 91 shows the towers in which the ammonia was oxidized to nitric acid at Muscle Shoals.

172. Physical Properties. Nitric acid is a colorless liquid, more than $1\frac{1}{2}$ times as heavy as water. The pure acid boils at 86°C . It fumes in moist air. Since the pure acid is unstable, the concentrated nitric acid of commerce is a



FIG. 91.—In these towers ammonia may be oxidized to form nitric acid.

water solution containing about 68% nitric acid. Such a solution boils at 120°C . A more dilute solution boils at a lower temperature and loses water, thus becoming more concentrated.

173. Chemical Properties. 1. *Stability.* When boiled or exposed to sunlight nitric acid decomposes, forming *water*, *oxygen*, and *nitrogen peroxid*.

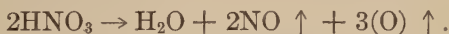


The acid is more stable in water solution. When the concentrated acid decomposes, part of the nitrogen peroxid dissolves in the acid imparting to it a yellow color. Nitric acid containing a large quantity of the peroxid in solution is red in color. It is known as *fuming nitric acid*. Phosphorus pentoxid takes water from nitric acid, leaving its anhydrid, N_2O_5 , a white crystalline solid.



2. *Acid Action.* Nitric acid is a very strong acid. It acts on many metals and on the oxids of metals forming nitrates. It neutralizes bases forming nitrates. The acid properties of nitric acid are more marked in *dilute* water solution.

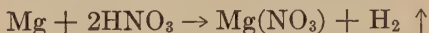
3. *Oxidizing Action.* In the paragraph on stability of nitric acid we learned that it liberates oxygen when it decomposes. It also breaks up in the presence of a reducing agent, forming *nascent oxygen*.



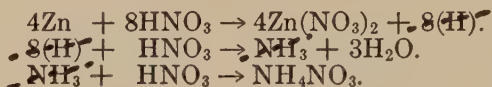
Since the oxygen is in the nascent state, nitric acid acts as a strong oxidizing agent. It readily oxidizes organic matter, such as hair, wool, and vegetable fibers. When charcoal is heated red hot and thrust into nitric acid it burns vigorously, the oxygen needed for combustion coming from the nitric acid. The products formed when the acid is reduced are very numerous. A partial reduction may occur, resulting in the formation of the various oxids of nitrogen, NO_2 , NO , or N_2O . Sometimes the nitric acid is more completely reduced to ammonia or ammonium nitrate. Nitric acid stains the skin yellow, forming *xantho-proteic acid*. On proteins it produces the same effect; therefore it may be used as a *test for protein*.

4. *Action with Metals.* The interaction between nitric acid and metals is varied and quite complicated. From the

general properties of acids we would expect to have hydrogen set free and a salt formed. But nitric acid is an oxidizing agent and many other products are often obtained. In fact the products depend upon the *concentration* of the acid and upon the *activity* of the metal. A very active metal like magnesium may liberate hydrogen from *very dilute* nitric acid.



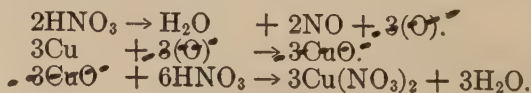
A metal like zinc may unite with nitric acid which is a little more concentrated to form products as represented by the following equations:



Unfortunately, there is no method known of stopping an equation at various steps to determine what intermediate products are being formed. The *end*-products may be analyzed, but we can only *estimate* the various steps. Thus we assume that the hydrogen that is first liberated reduces some of the nitric acid to ammonia, which in turn combines with more nitric acid to form ammonium nitrate. By using a dotted slanting line, let us cancel out all the products that are common to both sides of the *partial* equations as shown above and then combine the others into one equation as follows:



When a less active metal like copper interacts with *moderately* concentrated nitric acid, the reduction of the acid is not carried so far. Let us represent the possible reaction by *partial* equations:



By cancelling and combining these partial equations we have the *complete* equation,

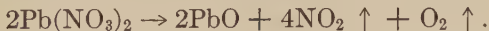


It is probable that the *nascent oxygen* formed when the nitric acid decomposes oxidizes the copper to copper oxid, which interacts with the excess acid forming water and copper nitrate. Such very inactive metals as gold and platinum are not attacked by nitric acid and aluminum only slightly. It attacks all other *common* metals.

174. Uses of Nitric Acid. 1. *Preparation of Nitrates.* Nitrates are salts of nitric acid; they are formed when nitric acid acts upon metals or metallic oxids, sodium nitrate being the only one that occurs extensively in nature. *All nitrates are readily soluble in water.* Sodium, potassium, and calcium nitrates are the most important representatives of this class of salts. They find extensive use in fertilizers and in making explosives. When heated, sodium and potassium nitrate lose one atom of oxygen and form *nitrites*.



With the exception of ammonium nitrate, other nitrates decompose as follows when heated:



2. *In Dye Industry.* Nitric acid is used for making aniline, which is the starting point for a large number of basic dyes.

3. *Making Explosives.* The old black gunpowder contained potassium nitrate; all the modern explosives are now prepared by the action of nitric acid upon such substances as glycerin, toluol, cotton, aniline, carboic acid, etc. A fuller discussion of explosives is reserved for a subsequent chapter. (See Chapter XXVIII.)

175. Nitrous Acid and Nitrites. We have seen that the nitrates of sodium and potassium lose 1 atom of oxygen when heated, forming the *nitrites*, NaNO_2 and KNO_2 . When sodium nitrite in dilute solution is treated with an acid, *nitrous acid* is formed. The acid is unstable, decomposing into water, nitric acid, and nitric oxid, NO . It is used extensively in making certain dye-stuffs. Nitrogen trioxid, N_2O_3 , is its anhydrid.



B. OXIDS OF NITROGEN

176. Oxids of Nitrogen. The valence of nitrogen is so varied that it is possible for the element to form five different oxids. *Nitrogen monoxid*, or *nitrous oxid*, has the formula N_2O ; *nitric oxid*, has the formula NO ; *nitrogen trioxid*, or *nitrous anhydrid*, has the formula N_2O_3 ; *nitrogen tetroxid*, commonly called *nitrogen peroxid*, has the formula NO_2 , or N_2O_4 ; *nitrogen pentoxid*, or *nitric anhydrid*, has the formula N_2O_5 . The anhydrids of nitrous and nitric acids have already been discussed. They are useful oxidizing agents.

177. Nitrous Oxid (N_2O). *a. Preparation.* Nitrous oxid, the gas used by dentists as an anesthetic, is commonly called "laughing gas." When ammonium nitrate is heated, it decomposes into water and nitrous oxid. The gas is usually collected by water displacement. The student should compare the equation for its preparation with that for making nitrogen.



b. Properties. Nitrous oxid is a colorless gas with a sweetish odor and taste. It is heavier than air and moderately soluble in water. It may be easily condensed to a liquid, in which form it is usually put on the market.

At ordinary temperatures nitrous oxid is stable, but at

increased temperatures it decomposes into nitrogen and oxygen. When decomposition occurs, the resulting mixture of gases (2 to 1) is richer in oxygen than the air (4 to 1). Hence nitrous oxid supports combustion better than air does, if the burning material has high enough temperature to decompose the gas into nitrogen and oxygen. A *glowing* splinter bursts into flame when thrust into a bottle of nitrous oxid. *Feebly* burning sulfur is not hot enough to decompose nitrous oxid, so it is extinguished by the gas. *Vigorously* burning sulfur, however, decomposes nitrous oxid and burns almost as well as in pure oxygen.

c. *Uses.* When nitrous oxid is used as an anesthetic, it produces a kind of nervous intoxication that makes a person unable to control his risibilities. Hence it is known as "laughing gas." After its discovery by Sir Humphry Davy, it became quite the vogue to administer this gas at evening parties as a source of amusement. When used by dentists air or oxygen is generally given at the same time.

178. Nitric Oxid(NO).

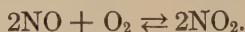
a. *Preparation.* When we studied the action of nitric acid on metals we learned that nitric oxid is produced when moderately concentrated nitric acid acts on copper. (See section 173.) The gas is collected by water displacement.

b. *Properties.* Nitric oxid is a colorless gas, slightly heavier than air. It is very slightly soluble in water.



FIG. 92.—The colorless nitric oxid unites with oxygen to form the reddish-brown nitrogen peroxid.

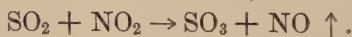
The most important chemical property of nitric oxide is its ability to combine directly with more oxygen when it is exposed either to the air or to oxygen. See Fig. 92. The following reaction is reversible:



Nitric oxide is quite stable. Although it is more than 50% oxygen it does not support ordinary combustion. Vigorously burning phosphorus is hot enough to decompose the gas, however, and phosphorus will continue to burn in nitric oxide.

Nitric oxide combines with certain salts such as ferrous sulfate, FeSO_4 . This reaction serves as a delicate *test for nitric acid or nitrates*. If we mix a concentrated solution of ferrous sulfate with *dilute* nitric acid, or a nitrate, and then add sulfuric acid by letting it run down the side of the tube, a *brown ring* is formed at the inter-surface between the heavy acid and the lighter solution above. The ferrous sulfate reduces the nitric acid, formed by the action of the sulfuric acid, to nitric oxide which then unites with the excess ferrous sulfate to form the reddish-brown ring.

c. Uses. The ease with which nitric oxide takes on oxygen from the air and then gives it up again in the presence of a reducing agent makes this gas a valuable *carrier of oxygen*. For example, nitric oxide forms the peroxide, NO_2 , upon exposure to air. The peroxide oxidizes sulfur dioxide as shown in the equation,



The nitric oxide that is produced at the same time may take on more oxygen and in turn oxidize more sulfur dioxide. This property of nitric oxide is used in the manufacture of sulfuric acid. (See section 244.)

179. Nitrogen Peroxide or Tetroxide, NO_2 . In the preceding section we learned that nitrogen peroxide is formed

when nitric oxid is exposed to the air. It may be formed by heating nitrates, sodium, potassium, and ammonium nitrates excepted.

At ordinary temperatures it is a reddish-brown gas, having a disagreeable suffocating odor. *This gas is very poisonous.* Its molecular weight shows that its formula is NO_2 . At low temperatures the color practically disappears and the molecular weight increases, showing that it has the formula N_2O_4 . Such *association of molecules at low temperatures and dissociation at higher temperatures* is not uncommon in chemistry. The reversible equation follows:



Nitrogen peroxid is unstable enough to support ordinary combustion very readily. It is very soluble in water, nitric acid being formed by such solution. See section 171.

Nitrogen peroxid is a very useful oxidizing agent.

SUMMARY

Nitric acid is prepared by heating a mixture of *sodium nitrate and sulfuric acid*.

Nitric acid is a heavy, colorless liquid; it boils at 86°C . In water solution the acid is fairly stable. In very dilute solution it may act as an acid. In concentrated solution it is a vigorous oxidizing agent. Nitric acid seldom liberates hydrogen when it acts on metals; it usually liberates *nitric oxid* or *nitrogen peroxid* and forms nitrates of the metal.

Nitric acid finds extensive use in the preparation of nitrates, in the dye industry, and in the manufacture of explosives.

Nitrogen forms a series of five oxids. *Nitrous oxid* is used as an anesthetic; *nitric oxid* is a carrier of oxygen; *nitrogen trioxid*, *nitrogen peroxid*, and *nitrogen pentoxid* are valuable oxidizing agents.

QUESTIONS

1. Why does nitric acid acquire a yellow color when exposed to sunlight?
2. Why would modern warfare be practically impossible without nitric acid?

3. State as many arguments as you can against the dismantling of the plant at Muscle Shoals, Alabama.

4. Since nitric oxid has a higher percentage of oxygen than nitrous oxid, explain why the latter is the better supporter of combustion.

5. How would you neutralize or remove acid stains on clothing? Does the method you suggest apply to spots made with nitric acid?

6. Given five unlabeled jars containing the following gases: oxygen, nitrogen, nitrous oxid, nitric oxid, and nitrogen peroxid. How would you identify each?

7. Nitric acid was formerly called *aqua fortis*. Can you see a good reason for such a name?

8. Why can not nitric acid be used for preparing hydrogen?

9. State the law that is exemplified by the oxids of nitrogen.

10. The colonists at Jamestown grew crop after crop of tobacco. Explain how they were robbing the soil.

11. Suppose you own a farm whose soil had been robbed of its fertility. How would you build it up again?

PROBLEMS

1. A sample of sodium nitrate is 90% pure. How many pounds of nitric acid can be made from one ton of the nitrate?

2. A sample of potassium nitrate is 90% pure. How many pounds of nitric acid can be made from one ton of the nitrate? If sodium nitrate and potassium nitrate were the same price per pound, which would you use if you were a manufacturer of nitric acid?

3. How many liters of nitric oxid can be prepared by the action of 252 gm. of nitric acid on an excess of copper?

4. If the air were 20% oxygen, in what proportions should the air and ammonia be mixed for the oxidation of ammonia to nitric acid?

CHAPTER XIX

CARBON

180. Occurrence of Carbon. Under the study of fuels we learned that coal, wood, and oils contain carbon. This element is found not only in fuels, but also in plant and animal tissues. When the potatoes scorch, or the meat burns, the presence of carbon is shown by the black color that is produced. In coal carbon is found *uncombined* or *free*, although it is also present in the form of hydrocarbons. Carbon is also found free in diamonds and in graphite.

181. Allotropic Forms. In our study of oxygen we learned that oxygen may absorb energy and become more active in the form of ozone. Carbon, too, may exist in different *allotropic* forms. (1) In a beautiful, crystallized form pure carbon exists in the *diamond*. (2) The grayish-black, greasy substance that is used in "lead" pencils is carbon in a different guise. Chemists call this form *graphite*. Graphite crystallizes in the form of hexagonal prisms. (3) Every one recognizes carbon in *charcoal*, *coke*, *lampblack*, and *bone-black*. These are all varieties of non-crystalline, or *amorphous* carbon.

182. Charcoal. Charcoal is prepared by the *destructive distillation* of wood. The wood is heated in closed retorts without access to air. Combustible gases, wood vinegar or acetic acid, and wood alcohol are among the by-products that are obtained, although various other products are obtained from certain kinds of trees. Charcoal is left in the retort as a residue. The charcoal tree of Fig. 93 shows some of the products obtained by distilling wood.

Charcoal is a porous, black, brittle solid. It is heavier than

readily with oxygen at higher temperatures. Thus it is an excellent reducing agent.

Since charcoal adsorbs gases it makes a good deodorizer. It is also used to decolorize certain liquids. To a much more limited extent than coke, charcoal finds use as a reducing agent and as a fuel.

183. Coke. Coke is made by the destructive distillation of soft coal. Prior to 1914 more than 75% of the coke made

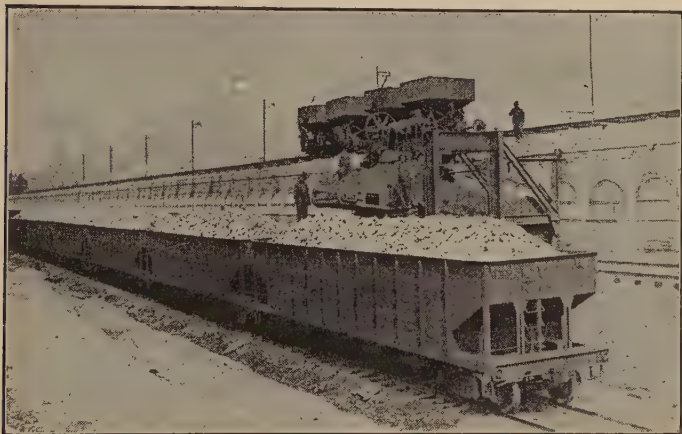


FIG. 94.—Over a half-mile of bee-hive coke ovens.

in the United States was manufactured in *bee-hive* ovens. See Fig. 94. In such an oven part of the coal with which it is filled is burned in order to supply the heat needed to drive off the volatile matter from the unburned portion. The by-products, gas, coal-tar, and ammonia, are all wasted in this process. It is estimated that the waste in 1913 of these by-products amounted to more than \$70,000,000.

Since the beginning of the War *by-product* ovens have been installed until at the present time about 70% of the coke is made in such ovens. The by-products from the coal are saved and the yield of coke is also increased about 10 or 15%.

See Fig. 95, which shows a battery of by-product ovens. Fig. 96 shows a net-work of pipes and condensers used in the recovery of by-products obtained in the distillation of soft coal.

Coke is a gray solid, harder and denser than charcoal. It burns with little flame. Coke is an *excellent reducing agent*.

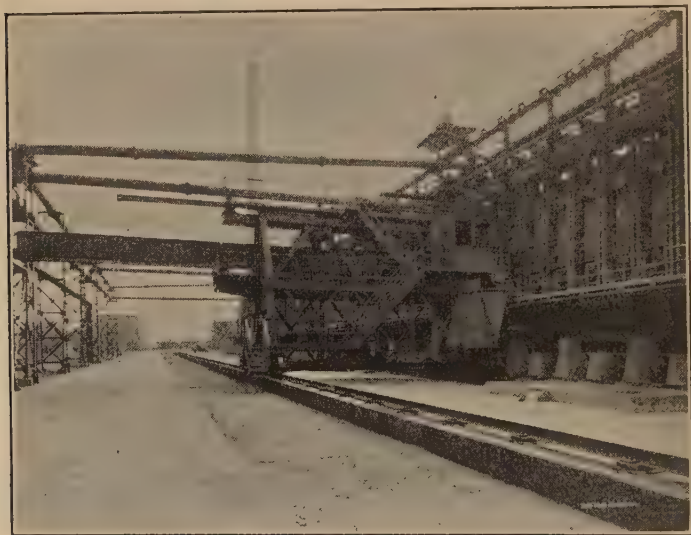


FIG. 95.—Battery of by-product coke ovens.

Millions of tons are used annually to take the oxygen from the ores of iron, copper, tin, and zinc.

184. Animal Charcoal. This form of amorphous carbon, commonly known as *boneblack*, is made by the destructive distillation of bones. It generally contains considerable mineral matter, 80% or more. In chemically treated bone-black, hydrochloric acid is used to dissolve the mineral matter, which is present as calcium phosphate.

Animal charcoal is used extensively for clarifying and decolorizing liquids, especially crude sugar solutions and oils.

185. Lampblack. When oil or gas is burned in an insufficient supply of air, soot or lampblack is formed. In making lampblack commercially the carbon is deposited on the cool surface of a revolving disc and then scraped off into bags.

Lampblack is a velvety powder, which finds use in making printer's ink, shoe polish, India inks, black varnishes, and



FIG. 96.—These towers, tanks, stills, and condensers conserve for one company 26,000,000 cu. ft. of gas per day; 18,000 gals. of benzol; 60,000 lb. of ammonium sulfate; 17,800 lb. of tar; and 4500 gals. of refined oil.

paints. This powder is also used as a “filler” in making automobile tires.

186. Gas Carbon is finely divided carbon that collects on the walls of the retorts used in making coal gas and coke. When it is pressed into a compact mass it becomes quite a good conductor of electricity. Gas carbon is used as the positive plate in dry cells and for making electric arc carbons.

187. Graphite. Graphite is a crystalline variety of carbon. It is soft, friable, and has a greasy feel. Its specific

weight is 2.25. Graphite is a good conductor of electricity. Heated in oxygen to a high temperature it burns forming carbon dioxid. The best graphite comes from Ceylon and Siberia although it is found in many other localities, among which are Austria, Germany, Canada, and the United States. *Artificial* graphite is now being made by heating hard coal or coke in an electric furnace.

Since graphite breaks up into small scales that readily slide over one another it is used as a *lubricant*, especially

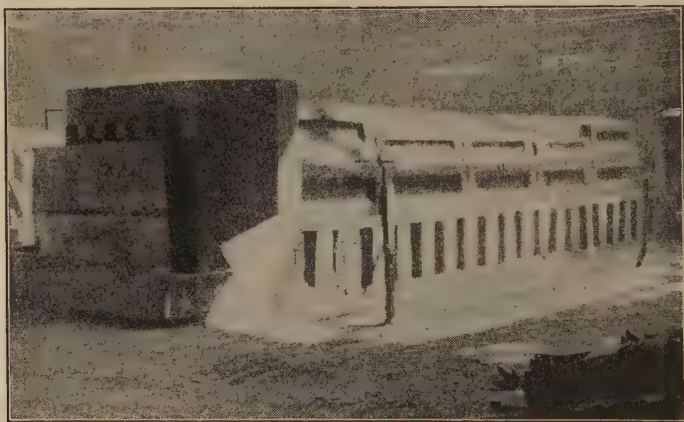


FIG. 97.—Electric furnace for making graphite.

where the temperature is high enough to decompose oils. It was Acheson, an American chemist, who learned how to make artificial graphite and carborundum in the electric furnace. See Fig. 97. The same man also devised a process of subdividing graphite into such fine particles that they do not settle when mixed with water or oil. Such deflocculated graphite makes a good lubricant. An emulsion of these particles with water is known as *aquadag* (*aqueous deflocculated Acheson graphite*); *oildag* and *gredag* are names given to suspensions of finely divided graphite in oil and grease respec-

tively. Graphite is sometimes used in smokeless powders to prevent gun erosion.

Graphite is used as an electrical conductor in the process of electrotyping and in the manufacture of electrodes. For use



FIG. 98.—A saw fitted with diamond teeth for sawing marble.

in electric furnaces graphite electrodes as large as 17 in. in diameter have been made.

Since graphite is very refractory it is used in making *crucibles*. For use in making steel the graphite is mixed with clay to form the crucible.

Graphite is often called *black lead*. It is used in making

lead pencils. The hardness of the pencil depends upon the amount of clay that has been mixed with the graphite.

188. Diamond. The diamond is also a crystalline form of carbon. It is the densest form of carbon, its specific weight being 3.5. It is one of the hardest substances known. When burned in oxygen it forms nothing but carbon dioxide, hence it is composed of pure carbon.

The value of the diamond as a gem depends upon its color and its high index of refraction, which is nearly 2.5. It is so cut that its brilliance will be increased by the play of colors from numerous facets. Low-grade diamonds are

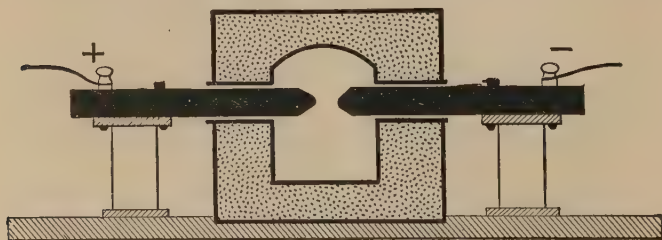


FIG. 99. A simple electric furnace.

used for cutting very hard materials. Saws fitted with diamonds to serve as teeth are used for sawing marble. See Fig. 98. The black diamond is used extensively by mining prospectors. The diamond drill is fitted with a steel shoe set with black diamonds. Ore prospectors and estimators use such a drill to cut through the hardest rock. The solid core which is cut out by the drill is brought to the surface where it may be examined or analyzed. Chip diamonds are pierced and then set in a brass disc to be used as dies for drawing very small wire. Tungsten wire which is to be used for electric light filaments is drawn through a small hole in such a diamond die. The finest wire has a diameter about $\frac{1}{6}$ that of the average hair. The carat is the weight unit used in the sale of diamonds. It is equal to 200 milligrams.

189. The Electric Furnace. In its simplest form the electric furnace consists of two carbon rods mounted in a block of refractory material. See Fig. 99. The carbon electrodes are brought together momentarily. At the point of contact the heat developed volatilizes the carbon, its vapor conducting the current as the rods are slightly separated. The temperature is exceedingly high, estimated at

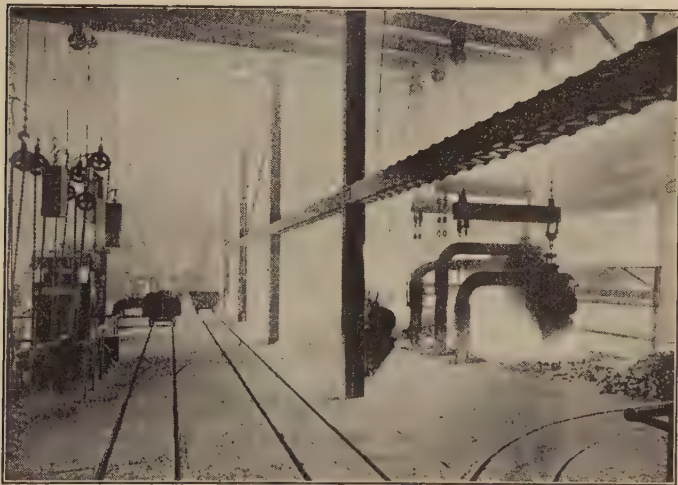


FIG. 100.—An electric furnace used for making calcium carbide.

3500° C. A large number of chemical reactions occur at this temperature that can not be brought about in any other way. The changing of hard coal into graphite when heated in the electric furnace has already been mentioned. *Carbon disulfid* and *carbon tetrachlorid* are also made in electric furnaces. We have already learned that Willson accidentally discovered a practical method of making *calcium carbide* when he heated lime and coke in an electric furnace. Fig. 100 shows a modern furnace used for making calcium carbide. The equation follows:



Carborundum, CSi , another product of the electric furnace, is made by heating sand and coke at a very high temperature. Considerable quantities of high-grade steel are made in electric furnaces.

Moissan succeeded in preparing artificial diamonds by the use of an electric furnace. By dissolving carbon in molten iron in an electric furnace and then cooling the surface quickly the shrinkage produces enormous pressure. Under such pressure the carbon crystallizes from its solution to form minute diamonds. The process is of no commercial value.

SUMMARY

Carbon is present in the air in the form of carbon dioxide; it occurs in all organic matter, both plant and animal.

Carbon exists in three allotropic forms: *amorphous carbon*, *graphite*, and the *diamond*.

Charcoal, *coke*, *gas carbon*, *boneblack*, and *lampblack* are all varieties of amorphous carbon.

Charcoal is prepared by the destructive distillation of wood, boneblack by the destructive distillation of bones, and coke by the destructive distillation of soft coal.

At the ordinary temperature all forms of carbon are inert; at higher temperatures they unite with oxygen to form carbon monoxide or carbon dioxide.

Carbon adsorbs gases readily and hence *deodorizes* solutions; it also *decolorizes* certain solutions. Since it is insoluble in ordinary solvents it makes a good pigment, being used for paints or lacquers and for inks.

Graphite is a soft, crystalline form of carbon that finds use in "lead" pencils, as a lubricant, for making crucibles, and as electrodes for electric furnaces.

Diamond is also a crystalline form of carbon. It is the hardest mineral known. The diamond is used as a gem and for cutting very hard substances.

The electric furnace is now used extensively for producing very high temperatures. *Artificial graphite*, *calcium carbide*, *carborundum*, and some *high-grade steels* are products of the electric furnace.

QUESTIONS

1. Why is it so difficult to remove stains made by printer's ink?
2. Why is carbon one of the most important elements?
3. What properties has graphite that make it useful for stove polishes?
4. Do you think graphite would be suitable for use in paints? Give a reason for your answer.
5. Why does a kerosene lamp often burn with a smoky flame? Suggest two remedies.
6. Is the name "lead" pencil a good one? Give a reason for your answer.
7. Name as many products as you can that are made in the electric furnace.
8. Why are the ends of telegraph poles often charred before being put in the ground?
9. How would you prove that the various allotropes of carbon are all composed of nothing but carbon?

CHAPTER XX

OXIDS OF CARBON—ILLUMINATING AND FUEL GASES

A. CARBON DIOXID

190. Occurrence. From our study of the atmosphere we know that the air contains carbon dioxid. This gas is exhaled by animals, and it is given off to the air when animals and plants decay. It is also a product of ordinary combustion.

191. Preparation. There are several ways of preparing carbon dioxid, of which three are given here:

1. *Burning Carbon.* When any one of the forms of carbon or any carbonaceous material burns, carbon dioxid is one of the products. If we use this method for preparing carbon dioxid, the gas that is formed will be impure, since it will be mixed with the constituents of the air and with other products of combustion.

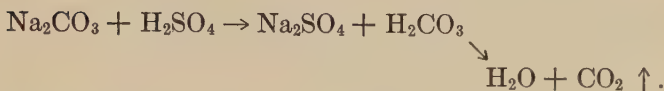
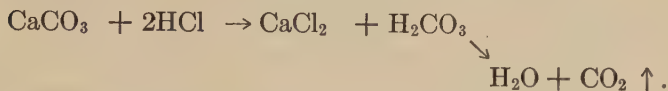
2. *Heating Carbonates (A Commercial Method).* When calcium carbonate, or limestone, is heated it decomposes as shown by the equation,



Most other carbonates decompose in an analogous manner, although the carbonates of sodium and potassium are exceptions.

3. *Action of Acids on Carbonates (Usual Laboratory Method).* Nearly all acids act readily upon carbonates, forming a salt of the acid used and the *unstable* carbonic acid. As the reaction proceeds, the carbonic acid breaks up into

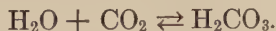
water and carbon dioxid, which escapes with *effervescence*. The gas may be collected by water displacement or by air displacement. The following equations are typical:



192. Physical Properties. Carbon dioxid is a colorless gas with a slight odor and taste. It is about $1\frac{1}{2}$ times as heavy as air, and frequently collects at the bottom of wells, mines, and caves. Before entering dry wells workmen often lower a lighted candle to see whether sufficient carbon dioxid is present to extinguish the flame. If the gas is present it is bailed out with buckets before the workmen enter. It is not poisonous, but animals die in it from suffocation. It is soluble in water. The gas may be rather easily liquefied; liquid carbon dioxid is put on the market in steel cylinders.

193. Chemical Properties. Carbon dioxid is a very stable compound. It neither burns nor supports combustion, although such metals as burning sodium or magnesium decompose it and continue to burn by uniting with the oxygen abstracted from the carbon dioxid.

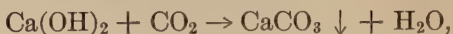
It is the anhydrid of *carbonic acid*. This acid is very weak and exists in water solution only.



Carbon dioxid interacts with the solutions of bases to form carbonates.



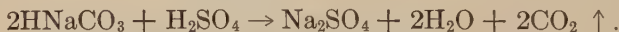
If we use calcium hydroxid (limewater) the calcium carbonate forms a white precipitate. This reaction,



forms a test for carbon dioxid. In a similar manner carbon dioxid unites with the oxids of some metals to form carbonates.

194. Uses of Carbon Dioxid. 1. *As a Plant Food.* From our study of the carbon dioxid-oxygen cycle we are familiar with the importance of carbon dioxid as a plant food. (See section 146.)

2. *As a Fire Extinguisher.* Since carbon dioxid does not burn it may be used to extinguish fires. In the type of extinguisher shown in Fig. 101, carbon dioxid is generated rapidly by the action of sulfuric acid on sodium bicarbonate, or baking soda. The equation is as follows:



When the extinguisher is turned bottom side up, the acid spills out and comes into contact with the baking soda solution. The pressure of the gas forces a stream of water and carbon dioxid bubbles into the fire.

2. *Carbonated Beverages.* Certain mineral waters are made effervescent by charging them with carbon dioxid under pressure. Effervescence occurs when the bottle is opened. Soda water is charged with carbon dioxid in the same manner. Since carbon dioxid is produced when sugar ferments, such beverages as champagne are charged with carbon dioxid during fermentation.

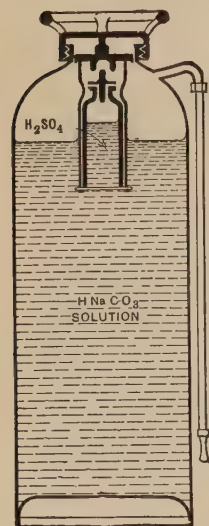


FIG. 101.—Carbon dioxide fire extinguisher.

3. *As a Leavening Agent.* Yeast causes sugar to ferment and carbon dioxid is liberated. As the bubbles of gas become entangled in the plastic dough they cause it to rise not only while they are being set free but also when they are heated during the baking (Law of Charles).

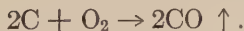
There are several ways of liberating the carbon dioxid. The action of yeast has been mentioned. Baking soda and baking powder are often used, because they liberate the gas more quickly. Baking soda liberates carbon dioxid when it is treated with sour milk, molasses, or cream of tartar.

Baking powders contain soda, starch, and some acid or acid salt. The starch keeps the powder dry, while the soda furnishes the carbon dioxid. The compound used to set the carbon dioxid free varies with the kind of baking powder. Some use tartaric acid and cream of tartar; others use calcium acid phosphate; while a third type of powder uses alum.

B. CARBON MONOXID

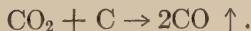
195. Introductory. We have already learned something about this treacherous poison in our study of fuels. It has taken the lives of many persons because fires were improperly banked, or because some one carelessly breathed the exhaust gas from a gas engine.

196. Preparation. 1. *Burning Carbon in an Insufficient Supply of Air.* When carbon burns in air or oxygen, carbon dioxid is formed. If there is not enough oxygen present to combine with all the carbon, then the following reaction occurs:



Of course the gas formed by incomplete combustion is impure, being mixed with other products of combustion.

2. *Reduction of Carbon Dioxid.* When carbon dioxid comes into contact with white hot carbon it is reduced to carbon monoxid.



Both these methods of preparing carbon monoxid are used on a large scale in the extraction of metals from their ores.

3. *Decomposition of Oxalic Acid (Usual Laboratory Method).* When oxalic acid, $(\text{COOH})_2$, is heated with sulfuric acid it breaks up as shown below:



The sulfuric acid dehydrates the oxalic acid which then splits up into carbon dioxid and carbon monoxid. This mixture may be separated by bubbling the gases through a solution of a base such as the hydroxid of sodium or calcium; the carbon dioxid unites with the base while the monoxid is unaffected and may be collected by water displacement:



197. Physical Properties. Carbon monoxid is a colorless, odorless, tasteless gas. It is slightly lighter than air, having the same density as nitrogen. Carbon monoxid is very slightly soluble in water. It is difficult to liquefy.

198. Chemical Properties. Carbon monoxid burns with a blue flame. The burning gas from hard coal consists largely of carbon monoxid. It is very poisonous since it unites with the red blood cells and makes them unable to carry oxygen. As small an amount as 0.1% is dangerous to life, and rapidly produces fatal results. One of the big problems for the engineers constructing the vehicular tunnel under the Hudson River is that of ventilation. The exhaust from the motor vehicles will contaminate the air rapidly, unless provision is made to change the air quickly. Canary birds are very susceptible to this poison and they have been used to test air in dug-outs, tunnels, and mines. The most

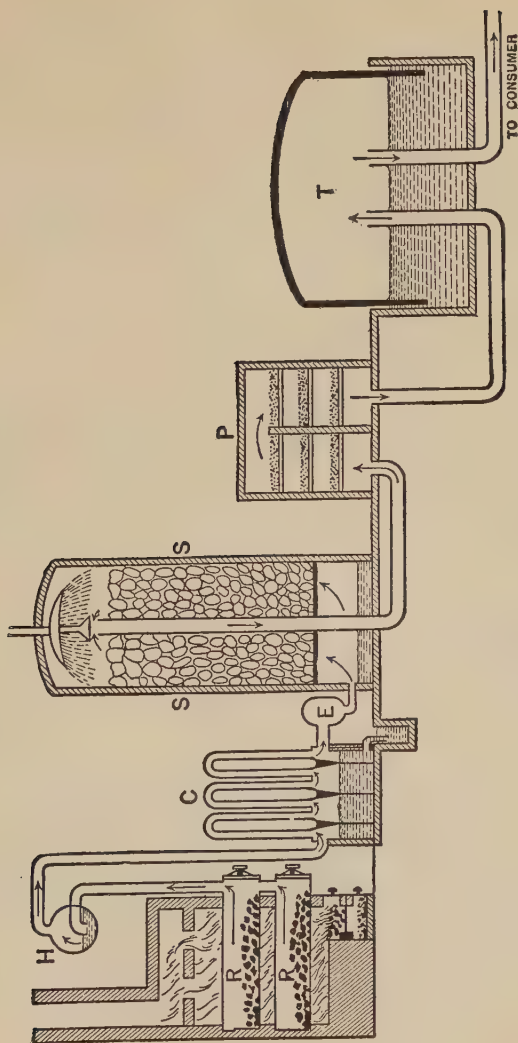
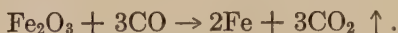
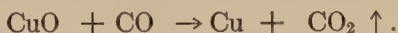


FIG. 102.—Diagram of a plant for making coal gas.

important chemical property of carbon monoxid is its action as a *reducing agent*.

199. Uses. Carbon monoxid has two very important uses: (1) *As a reducing agent*; (2) *as a fuel*.

In extracting metals from their ores the coke, charcoal, or coal forms carbon monoxid. The monoxid unites with the oxygen of the ore to form carbon dioxid and the metal. The following equations are typical of such reduction:



Unless the carbon monoxid that forms in the burning of hard coal is oxidized, more than half the fuel value is wasted. Carbon monoxid is present to some extent in coal gas and it forms one of the chief constituents of water gas and producer gas.

C. FUEL GASES AND ILLUMINATING GASES

200. Coal Gas. Coal gas is made by heating soft coal in retorts. Fig. 102 shows the arrangement of a plant for making coal gas. The retorts, *R*, are usually arranged one above the other to economize fuel. From the retorts the gas passes through a dip-pipe into the hydraulic main, *H*; next it goes to the condenser, *C*, where it is cooled considerably and the tar and ammonia partially removed. An exhauster, *E*, keeps the gas moving in the proper direction and regulates the pressure in the retorts. In the scrubbers, *S*, the traces of tar are mechanically removed and the gas thoroughly washed by a spray of water. In the purifiers, *P*, layers of lime or iron oxid, or sometimes both, are used to remove sulfur compounds and carbon dioxid. The purified gas then passes to a storage tank, *T*.

From a ton of good gas coal about 10,000 cu. ft. of gas, 1200 to 1400 lb. of coke, 120 lb. of coal tar, and 20 gal. of

201. Water Gas. When steam comes into contact with white hot coke or hard coal, hydrogen and carbon monoxid are formed.



The products are both combustible and the mixture is known as *water gas* or *blue gas*.

Water gas is made commercially by forcing a blast of hot air through coal or coke until it is heated white hot.

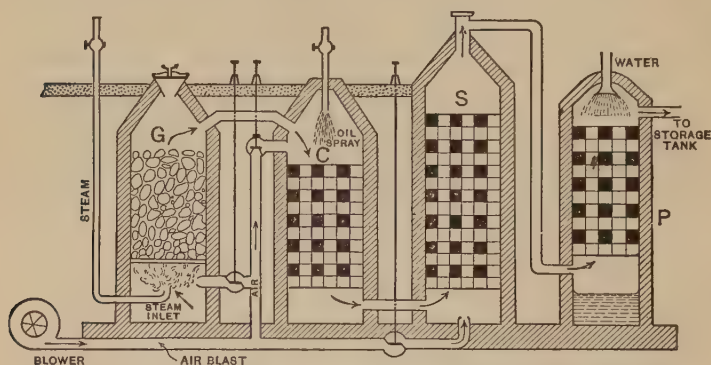


FIG. 104.—Diagram of a plant for making water gas.

The air blast is then shut off and steam passed through the coke to form the hydrogen and carbon monoxid. Air and steam are then used alternately. Since both hydrogen and carbon monoxid burn with little color, the water gas must be enriched if it is to be used for illuminating purposes. As the water gas comes from the generator, *G*, Fig. 104, it enters the carburetor, *C*. Here a spray of oils consisting of hydrocarbons is introduced. The mixture of these oils with the gas then enters the superheater, *S*, which decomposes them into permanent gases which do not condense to a liquid when the gases are stored. Some of the oils in passing through the superheater are “cracked” or broken up into simpler

molecules. After passing through the lime purifiers, *P*, the gas goes to the storage tank.

Water gas has a high heat value. When enriched it forms a good illuminating gas. The high percentage of poisonous carbon monoxid forms the chief objection to its use. The impurities consist of ammonia, hydrogen sulfid, and carbon dioxid, the same as those found in coal gas.

202. Producer Gas. A cheap gas used for industrial purposes is made by forcing a blast of hot air through a deep layer of coal or coke.

See Fig. 105. Sometimes a little steam is introduced. The inflammable gas is carbon monoxid. Although this fuel gas contains about 60% of nitrogen, yet it burns with quite a hot flame. Producer gas is used as a fuel in making glass, steel, pottery, etc.

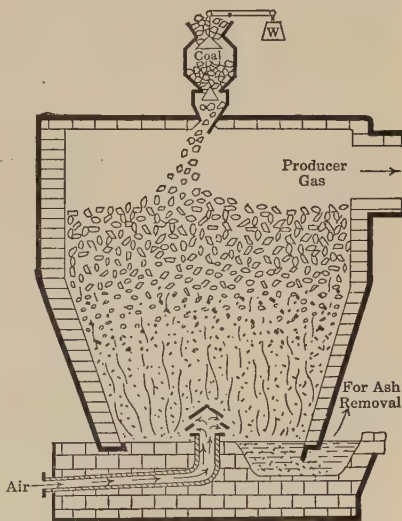


FIG. 105.—Gas producer.

oil are heated to a high temperature, about 1000° C., to “crack” the molecules and form permanent gases. Pintsch gas is compressed and sold in steel containers. It is used to some extent for lighting railway coaches.

2. *Blaugas* is also an oil gas. In this process the oil is not heated over 550° to 600° C. in order to avoid “cracking” the molecules. After the gas is washed and purified in the usual manner, it is subjected to a pressure of nearly 100

atmospheres. Under this high pressure some of the hydrocarbons liquefy; others that are more gaseous remain dissolved in the liquid hydrocarbons as long as the high pressure is maintained.

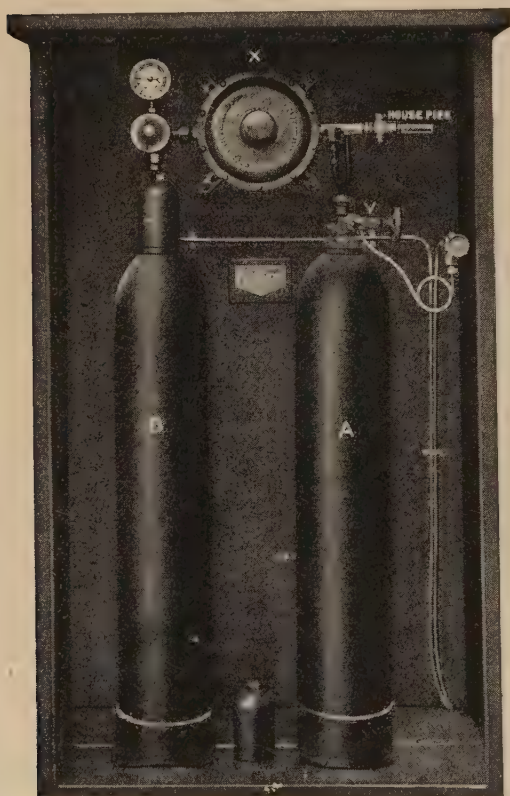


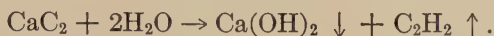
FIG. 106.—Blaugas cylinders. Pipe at right leads to underground expansion tank.

These liquid hydrocarbons are delivered to the consumer compressed in strong steel cylinders. When the valve, V, is opened the hydrocarbons vaporize and enter an expansion tank which is placed underground. Fig. 106. In this expansion tank the gas is under a pressure of about 50 lb. to the square inch. Before it is delivered to the burners it passes through a second reducing valve, X, to lower the pressure to about $\frac{1}{2}$ lb. per square

inch. Blaugas gives a luminous flame. It has a high heat value, and its explosive range is lower than that of most gases.

It is especially suitable for use in rural districts where connection with the city gas supply is impracticable.

204. Acetylene. Acetylene, C_2H_2 , is formed when water interacts with calcium carbid.



Generators of sufficient size to supply dwelling houses and stores are in use. The powdered carbid is dropped into the



FIG. 107.—Welding with oxy-acetylene blow-pipe. A completed weld shown at the right.

water with sufficient rapidity to secure a steady evolution of the gas.

Acetylene is a colorless gas with a peculiar odor. When a special burner like that of Fig. 41 is used, acetylene burns with an intense white flame similar to sunlight. Unless provision is made for mixing some air with acetylene before it is burned, the flame is very sooty and smoky.

In the making of acetylene, heat is absorbed. The reaction is endothermic, as represented by the following thermal equation:



When acetylene is burned, we get all the heat from the burning carbon and the oxidation of the hydrogen, *in addition* to the heat that was absorbed during the formation of the acetylene.



Thus the acetylene flame made by using the oxy-acetylene blowpipe, is the hottest that can be produced, its temperature being estimated at from 2700°C. to 3700°C. This blowpipe is used for welding, Fig. 107, and for cutting wrought-iron and steel plates or scrap of any kind. The tip of the flame is so hot that when it is drawn over the metal, it melts and burns the material



FIG. 108.—Crankshaft roughed out by the use of the oxy-acetylene flame.

in its path. It has been used by divers in cutting up submerged wrecks. Fig. 108 shows a piece of steel over 10 in. thick that was cut by means of the oxy-acetylene flame.

Since heat is absorbed when acetylene is formed, the gas may explode without oxygen. Such an explosion occurs only when the gas is compressed. For this reason acetylene can not be compressed to a liquid and marketed in the usual manner. It may be safely dissolved in acetone under pressure. The *prest-o-lite* container is filled with asbestos which is soaked with acetone. The acetylene is then forced into the

tank under pressure. See Fig. 109. Cylinders made by other companies are similar in construction.

205. Explosion of Gases and Explosive Range.

We have learned that hydrogen and oxygen explode violently when a mixture of the gases is ignited. In fact any combustible gas, when mixed with air or oxygen, explodes when heated to the kindling temperature of the gas. Combustible liquids that vaporize readily also form explosive mixtures with air. Gasoline, alcohol, ether, and kerosene are examples. In any such mixture, the explosion is most violent when the gases are mixed in the ratio of their combining volumes. From the preceding section, we conclude that acetylene will explode most violently when 2 volumes of the gas are mixed with 5 volumes of oxygen, or with 25 volumes of air.

While the proportions given above will produce the most dangerous explosion, yet other mixtures of air and acetylene will explode. In fact any mixture of these two gases containing from 3 to 30% acetylene is explosive. Hydrogen has a wide *explosive range*, since any mixture of hydrogen and air containing from 10 to 66% of hydrogen explodes violently. The explosion is most violent when the mixture contains 29% hydrogen.



FIG. 109.—
Prest-O-lite
tank. (Sec-
tional.)

ANALYSIS OF GASES (C. D. JENKINS, MASS. STATE REPORTS)

	Coal gas	Water gas (enriched)	Water gas	Oil gas
Candle-power.....	17.5	25		65
Illuminants.....	5	16.6		45
Marsh gas.....	34.5	19.8	1.0	38.8
Hydrogen.....	49	32.1	52	14.6 Ethane
Carbon monoxid.....	7.2	26.1	38	
Nitrogen and carbon dioxid...	4.3	5.4	9.0	1.1

For determining candle-power 5 cu. ft. of gas are burned per hour.

206. Cyanogen and Cyanids. Cyanogen is a colorless gas that burns with a blue flame. It may be prepared by heating cyanids, such as mercuric cyanid, $\text{Hg}(\text{CN})_2$. Its formula is C_2N_2 . The gas is exceedingly poisonous.

Hydrogen cyanid, HCN , is a volatile liquid boiling at 26°C . Its water solution is called *prussic acid* or *hydrocyanic acid*. It is one of the most poisonous substances known. Its vapor finds some use in destroying insects. Its most important salts are the *cyanids of potassium and sodium*. These compounds find extensive use in extracting gold from its ores, and in electroplating.

SUMMARY

Carbon dioxid may be prepared by burning carbon, by heating carbonates, or by the action of an acid on a carbonate.

Carbon dioxid is a heavy, colorless gas, fairly soluble in water. In water solution it forms carbonic acid. Carbon dioxid is stable; it neither burns nor supports combustion.

Carbon dioxid is used: (1) *in carbonated waters*; (2) *as a leavening agent*; (3) *as a plant food*; (4) *to extinguish fires*.

Carbon monoxid is a reduction product of carbon dioxid; it may be prepared by the incomplete combustion of carbon; or by heating oxalic acid with sulfuric acid.

It is colorless and odorless; it is intensely poisonous. Carbon monoxid burns with a blue flame. It is an excellent *reducing agent*.

Fuel and illuminating gases are made by the destructive distillation of soft coal and oil; water gas is made by blowing steam through hot coke; and acetylene gas by the action of water on calcium carbid.

At high temperatures nitrogen combines with carbon to form cyanogen, a very poisonous gas. With hydrogen, hydrocyanic acid is formed.

QUESTIONS

1. Can kerosene be substituted for gasoline for use in gas engines? Give reason for your answer.

2. Why might a block in traffic in the new vehicular tunnel under the Hudson River be dangerous?

3. How would you distinguish carbon dioxid from nitrogen? Carbon monoxid from hydrogen? Nitrous oxid from oxygen?

4. Devise a test for a carbonate.
5. Is it necessary to enrich water gas with oils if it is to be used for fuel only? If it is to be used for illumination with the Welsbach mantle?
6. Why is water gas somewhat more dangerous to inhale than coal gas?
7. A stick of sodium hydroxid slowly changes to a white powder when it is exposed to the air. What chemical change is taking place?
8. Name the most important reducing agents that we have studied.
9. Name several oxidizing agents that we have studied.
10. Try to find a reason for using hydrochloric acid in preference to sulfuric acid in preparing carbon dioxid from calcium carbonate.
11. When a bottle of limewater is left unstoppered, a white ring is formed at the surface of the liquid. Explain. How would you clean such a bottle?
12. Formic acid has the formula HCOOH . What gas would you expect to have liberated by the action of sulfuric acid on formic acid?

PROBLEMS

1. How many grams of sodium bicarbonate will be needed to liberate 10 liters of carbon dioxid?
2. How many liters of oxygen would be needed for the complete combustion of 100 liters of acetylene? How many liters of air?
3. How many pounds of calcium carbonate will be needed to prepare 320 lb. of carbon dioxid?

CHAPTER XXI

THEORY OF SOLUTION—IONIZATION

207. Introductory. Quite often reference has been made to the part that water plays in chemical reactions. We know that a gas engine works better when there is considerable moisture in the air. Experiment seems to show that hydrogen and oxygen can not be made to explode unless a *trace* of moisture is present. Baking powder does not deteriorate if it is kept dry, but chemical action begins at once when the powder is put into water. Thus water seems to be a general

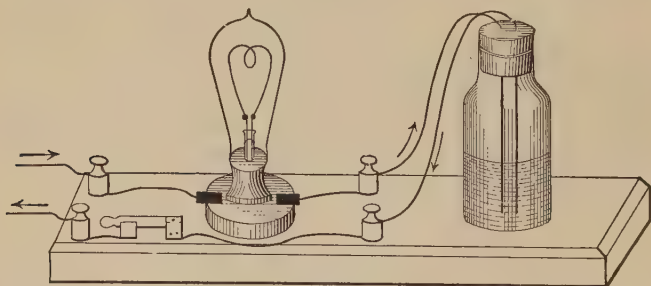


FIG. 110.—Apparatus used to test the conductivity of solutions.

catalyst in chemical reactions. For decades chemists were puzzled to account for such behavior of substances in water solution.

There are other problems, too. (1) If we use the apparatus shown in Fig. 110, we may test the conductivity of certain substances. Pure water is a non-conductor and does not let enough electricity through the apparatus to light the lamp. If we add a few drops of hydrochloric acid to the water in the

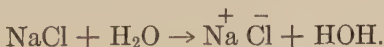
bottle and then close the circuit, the lamp glows brightly. Other acids behave in the same manner, although in most cases the lamp does not glow so brightly, showing that most acids do not conduct the current so well as hydrochloric. In the same manner we may test other compounds. We find that *acids, bases, and salts* in water solution are conductors, or *electrolytes*. The addition of such substances as sugar, alcohol, ether, or glycerin does not make the solution a conductor. Such substances are *non-electrolytes*.

(2) When we studied the effect of the solute on the freezing point and boiling point of solvents, we learned that Raoult's laws do not apply to acids, bases, or salts. In fact *electrolytes lower the freezing point almost twice as much as non-electrolytes*. They also raise the boiling point abnormally.

(3) *Electrolytes are more active chemically than non-electrolytes*. They generally act more rapidly and more energetically. These irregularities, in addition to others beyond the scope of this book, are difficult to explain. Probably the most plausible and the most generally accepted explanation of these facts is the *theory of ionization*.

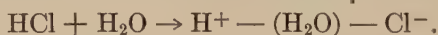
208. Ionization Theory. When Arrhenius, a Swedish chemist, proposed his theory of solution in 1887, he met with ridicule and scorn. Now, less than 40 years later, many chemists consider his ionization theory the greatest contribution to theoretical chemistry within the last century.

This theory of solution assumes that electrolytes in solution are *dissociated* into *ions*. An ion is an atom or group of atoms that carries an electric charge. To illustrate, suppose we dissolve sodium chlorid in water. Part of the sodium chlorid molecules dissociate into sodium ions and chlorid ions. The sodium ion carries a positive charge; the chlorid ion, a negative charge. The following *ionic* equation shows the manner of dissociation:



Some of the sodium chlorid molecules are not dissociated, but the percentage that dissociates increases as the solution becomes more dilute. Concentrating a solution by evaporating the water decreases the number of ions present, the solid salt being again obtained by evaporating to dryness. Water itself is *very* slightly ionized, forming positive hydrogen ions and negative hydroxyl (OH) ions.

In the electrical conception of valence it is assumed that one hydrogen atom may *lose* an electron and a chlorin atom may *gain* one. Electrical attraction is believed to be the cause of the chemical affinity, or bond, between H^+ and Cl^- in the formation of hydrogen chlorid, HCl. In *solution* the water in some unknown way seems to weaken or loosen (dissociate) the attractive force between the atoms. We may picture the water as an ionizing agent in the following manner:



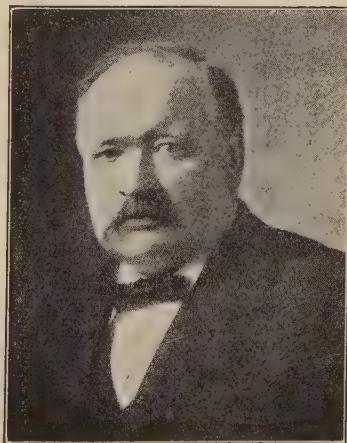
209. Ion and Atom. The opponents of the ionization theory state that if dissociation occurs in solution, as in the case of sodium chlorid, the sodium would attack the water forming sodium hydroxid and that the chlorin would color the solution yellow. But Arrhenius answers: "Is it not possible that an atom which carries an electric charge may have different properties from an atom which is not so charged?" We know that oxygen, for example, absorbs energy and changes to ozone, an allotrope having very different properties. *An ion is defined as an atom or a group of atoms that carries an electric charge.* When an atom loses its electrical charge, it has all the properties of the atom. As soon as the sodium ion gives up its positive charge it behaves in every way like a sodium atom. The same is true of the chlorin ion. Since there are the same number of positive charges as negative charges in a solution, there is no sign that the solution is electrically charged. Electricity manifests



(Permission of *Popular Science Monthly*.)

Charles Martin Hall (1863–1914) was an American inventor. While a student at Oberlin College he became interested in aluminum and began his research work in an effort to extract the metal at a lower cost. The reduction of aluminum oxid is difficult and the ore is not easily fused. Hall discovered that it dissolves readily in cryolite, a compound that is readily fusible. From such a solution aluminum may be obtained by electrolysis. Hall was awarded the Perkin medal in 1911.

Svante Arrhenius (1859—) is a Swedish physical chemist. In 1891 he was made Professor of Chemistry at the University of Stockholm. In 1887 he proposed the modern theory of the dissociation of electrolytes in solution. His ionization theory has done much to explain many observations over which chemists had long puzzled. He was awarded the Nobel prize in 1903.



(Permission of *Current Opinion*.)

itself only when there is an *excess* of one kind of electrical charge.

210. Ionization of Acids. All acids contain hydrogen. When they ionize the hydrogen ion is positive. The following examples are typical:



An acid may be defined as a compound that forms positive hydrogen ions in water solution.

From the above definition the *strength* of an acid would appear to depend upon the number of hydrogen ions present in a given volume of the solution. The student must not confuse the terms *strong* and *concentrated* as applied to acids. Dilute hydrochloric acid contains more hydrogen ions than concentrated acetic acid, because it ionizes so much more completely. Nitric acid is also a very *strong* acid. In the concentrated acid (68%) fewer than 10% of the HNO_3 molecules are ionized. When the acid is diluted with water until only 6% of the solution is made up of nitric acid molecules, more than 80% of the molecules are ionized. In the case of the *weak* acetic acid less than 0.5 of 1% of its molecules are ionized in a 6% solution. *Dry* hydrogen chlorid does not have acid properties. One hundred per cent nitric acid does not have acid properties. *These compounds act as acids only when they are in water solution, and the strength of the acid depends upon the concentration of the hydrogen ion.*

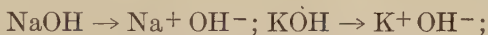
Quite often students get the erroneous idea that the more we dilute an acid, the stronger it becomes. Such is not the case, for 100 c. c. of a 50% acid in which 10% of the molecules are ionized will have more hydrogen ions than the same volume of 2% acid in which 95% of the molecules are ionized. Making a solution more dilute increases the *degree of ionization*, but it does not necessarily increase the number of hydrogen ions per cubic centimeter. Increasing the temperature of a solution also increases the degree of ionization.

Sulfuric acid does not ionize quite so readily as nitric or hydrochloric acid, and it is really a *weaker* acid, although because of its high boiling point it decomposes salts of either nitric or hydrochloric acid. Sulfuric acid undergoes two stages of ionization as follows, the first one much more readily:



Thus it is possible for sulfuric acid to form two different kinds of salts: (1) *acid salts*, in which the HSO_4 radical is present; (2) *normal salts*, in which the SO_4 radical is present.

211. Ionization of Bases. When bases ionize the metallic ion carries the positive charge and the hydroxyl $(\text{OH})^-$ ion is negative. For example,



In the last case we write 2OH^- and not $(\text{OH})_2^-$, since there are two negative hydroxyl ions. *A base may be defined as a compound that forms negative hydroxyl ions when it is in water solution.*

The strength of a base depends upon the concentration of the (OH) ion. Sodium hydroxid and potassium hydroxid are the strongest bases known. Ammonium hydroxid of equal concentration contains only about 4% as many (OH) ions; it is therefore a weak base.

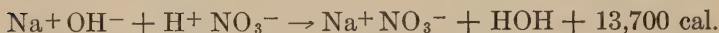
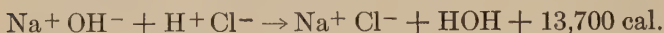
212. Neutralization. From the following ionic equation representing neutralization,



we see that the hydrogen ion of the acid unites with the hydroxyl ion $(\text{OH})^-$ of the base to form *non-ionized* water. Neutralization may be briefly defined as the union of the positive ion of an acid with the negative ion of a base to form water. The salt that is formed ionizes in the water, since

soluble salts usually have a high degree of ionization. A *salt* may be defined as a compound formed by the union of the positive ion of a base with the negative ion of an acid.

It is interesting to note that the amount of heat liberated by neutralizing *one mole* of hydrochloric acid is the same as that set free when one mole of nitric acid or one mole of hydrobromic acid is neutralized.



This is also the heat of formation of one mole, 18 gm., of water by neutralization. The neutralization of sulfuric acid, $2\text{Na}^+ 2\text{OH}^- + 2\text{H}^+ \text{SO}_4^{=}$ $\rightarrow 2\text{Na}^+ \text{SO}_4^{=} + 2\text{HOH} + 27,400$ calories,

forms *two moles* of water and *twice* as much heat is liberated.

213. Electrolysis. Keeping in mind the ionization theory, let us see how well it has answered some of the problems raised in section 207. We find by experiment that acids, bases, and salts are fair conductors of electricity when in solution, but not in the *dry* state.

In Fig. 111 we have represented a solution of copper sulfate. As the salt dissolves, some of the molecules dissociate. Since

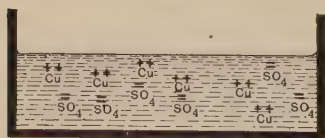
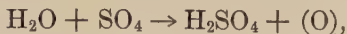


FIG. 111.—Dissociation of copper sulfate into its ions.

copper is bivalent, each copper ion (Cu^{++}) carries two plus charges; each sulfate group ($\text{SO}_4^{=}$) carries two minus charges.

Suppose we introduce into the solution two platinum strips, or carbon rods, and connect them to a battery as in Fig. 112. Since the rod A is connected to the positive plate of the battery it is charged positively; it is called the *positive electrode*, or *anode*. The rod B which is connected to the negative plate becomes negatively charged; it is called the

negative electrode, or cathode. Since like charges repel each other and unlike charges attract, the copper ions will go to the cathode. There they have their charge neutralized and are deposited on the cathode as a smooth coating of metallic copper. The sulfion (SO_4^-) is attracted to the anode; when its charge is neutralized, the SO_4 radical combines with the hydrogen of water,



forming sulfuric acid and liberating oxygen.

Electrolysis is the separation of a compound into its constituents by means of an electric current. The student should remember that dissociation occurs before the electrodes are introduced; the electric current separates the ions, the positive going to the cathode and the negative to the anode. The ions really conduct the current through the solution. Thus electrolytes are conductors because they dissociate into ions which migrate through the solution by attraction or repulsion. Non-electrolytes do not ionize and are therefore non-conductors.

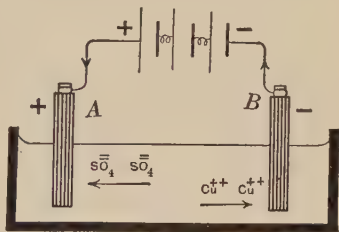


FIG. 112.—Electrolysis of copper sulfate.

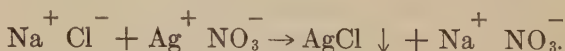
Electrolysis is a very important process in physical chemistry. By this process storage batteries are charged, certain elements are isolated, others are purified, and metals are electroplated.

214. Why Electrolytes Affect the Freezing Point and Boiling Point Abnormally. We know that one mole of a substance in 1000 gm. of solvent lowers the freezing point of a solvent 1.87°C . The freezing point will be lowered twice as much if two moles are dissolved. Since there are twice as many molecules in the second solution, it seems apparent

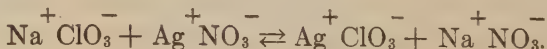
that the amount of lowering of the freezing point is directly proportional to the number of molecules or particles in the solution. Suppose we use as solute an electrolyte like sodium chlorid. If all its molecules *dissociate* there will be twice as many particles as before and we would expect to have the freezing point lowered 3.74°C. , or twice as much, per mole of solute. In reality, the freezing point is not lowered quite twice as much by such an electrolyte, because it is not 100% ionized.

Since calcium chlorid, CaCl_2 , furnishes three ions, one of calcium and two of chlorin, it seems reasonable to suspect that it would lower the freezing point of a solvent *three* times as much as a non-electrolyte of the same concentration. Careful experiments show that in very dilute solutions of calcium chlorid, when the ionization is nearly complete, the fact is in close accord with the theory.

215. Chemical Tests are Tests for Ions. It seems natural to expect that chemical action will take place more readily in solution if the molecules are *dissociated*. Their freedom in rearranging themselves is much greater, and we would expect ions to be more active than molecules. When we make tests in the laboratory, we test for ions and not for atoms or molecules. When we add to a solution of sodium chlorid a few cubic centimeters of silver nitrate solution the following reaction occurs:



The undissociated silver chlorid comes down as a white precipitate. Insoluble silver chlorid is always precipitated when silver nitrate is added to a solution of a chlorid. That this test is not a test for *chlorin* may be shown by adding a few cubic centimeters of silver nitrate to a solution of sodium chlorate.



Chlorin is present in sodium chlorate but no precipitate is formed with the silver nitrate. If any reaction occurs, all the substances ionize and remain in solution. Therefore silver nitrate forms a precipitate with any *chlorid* ion, but not with a *chlorate* ion. Silver nitrate is a test for Cl^- , but not for Cl , or ClO_3^- .

Anhydrous copper sulfate is white; the hydrated salt or a solution of the salt is blue in color. Since soluble copper salts give a blue solution we may infer that the blue color is due to the copper ion. In a similar way it may be shown that the ferrous ion is green, while the ferric ion is reddish-brown. Cobalt salts are pink in water solution when ionized, but a large number of them become blue when they are dehydrated.

The theory of ionization explains the fact that such mixtures as baking powder, effervescing powders, etc., do not act in the dry state, but that a chemical change begins as soon as water is introduced, thereby causing dissociation.

216. Valence of Ions. From the equations that have been given showing ionization, it is easy to see that the valence of an ion is equal to the number of electrical charges the ion carries. Hydrogen is capable of losing one negative charge or electron, and thus has a positive valence of 1; aluminum has the ability to lose three electrons, hence it has a positive valence of 3. The number of electrons a negative ion can gain, or acquire, determines its valence.

217. Ionizing Agents. Ionization occurs very readily in water solution. It does not occur so readily in most other solvents. Hydrogen chlorid does not act like an acid when dissolved in toluol since ionization does not occur. Ionization does not occur readily in such solvents as toluol, ether, and benzol.

Heat may produce ionization. Gases that are heated to a high temperature become fair conductors of electricity since

ionization takes place to some extent. Heating a solution increases the degree of ionization of the solute.

Fused or melted salts are ionized to some extent. Dry sodium chlorid is a poor conductor. The fused salt is quite a good conductor. Considerable use is made of the fact that ionization occurs when the salt is melted, especially in the electrolysis of compounds whose elements tend to unite readily with water, or of those compounds which are insoluble in water.

SUMMARY

An electrolyte is a compound whose water solution is a good conductor of electricity. *Acids, bases, and salts are electrolytes.* Such substances as alcohol, ether, and sugar are *non-electrolytes*. Their solutions are non-conductors.

The ionization theory assumes that *electrolytes are dissociated into ions in water solution*. An ion is an atom or a group of atoms carrying an electric charge.

An acid is a compound whose water solution contains hydrogen ions; its strength depends upon the concentration of the hydrogen ion.

A base is a compound whose water solution contains hydroxyl (OH) ions; its strength depends upon the concentration of hydroxyl ions.

Neutralization is the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water.

The ionization theory offers an explanation of the *conductivity* of certain solutions; it shows why electrolytes affect the *freezing point* and *boiling point abnormally*; and it is the best explanation offered for the *activity* of electrolytes in solution.

QUESTIONS

1. Why do we call the solution of hydrogen sulfid a weak acid and the solution of hydrogen chlorid a strong acid?

2. What is an electrolyte? How could you determine whether glycerin is an electrolyte?

3. Write ionic equations to show the neutralization of nitric acid by calcium hydroxid; of sulfuric acid by calcium hydroxid.

4. Define acid, base, salt, and neutralization from the standpoint of the theory of ionization.

5. Cold, concentrated sulfuric acid does not act on zinc to liberate hydrogen, but dilute sulfuric acid does. Explain.

6. From a consideration of the theory of ionization explain what happens when an electric current is passed through a solution of sodium chlorid.

7. Substances coated with a solution of a cobalt salt show color changes depending upon the amount of moisture in the air. Explain.

8. What is the difference between the hydrogen ion and the hydrogen atom? What is the difference between the hydrogen atom and the hydrogen molecule?

9. Which do you think would be the better conductor, seawater or distilled water? How do their freezing points compare?

10. Is dry hydrogen chlorid gas an acid? Is liquid hydrogen chlorid an acid? How would you treat hydrogen chlorid to give it acid properties?

CHAPTER XXII

EQUILIBRIUM AND REVERSIBILITY

218. Introductory. We know that many substances are very active chemically when in solution. We have also observed that some chemical reactions run to equilibrium or are reversible, while others run to completion in *one* direction only. It will be of interest to inquire why this is true. When we mix solutions of silver nitrate and sodium chlorid,



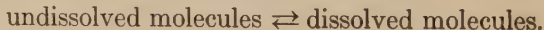
the reaction runs to completion in the direction shown by the arrow.

If we mix solutions of potassium nitrate and sodium chlorid,



the chemical reaction is reversible and it runs to equilibrium.

219. Equilibrium. Before we study the foregoing examples, let us refer to some simpler cases of equilibrium. We prepare a saturated solution by shaking an excess of the solute with the solvent. At first molecules of the solvent go into solution rapidly. But it seems reasonable to assume that some of these molecules may return to the undissolved mass. As the solution becomes more concentrated, a greater number of molecules will return per second. When the number of molecules returning to the undissolved mass per second is the same as the number of molecules going into solution per second, the solution is said to be saturated. In such a *physical* solution we have the following equilibrium,



In a similar manner we have equilibrium between the *dissociated* and *undissociated* molecules in a *chemical* solution. It is believed that there is *ionic equilibrium* in a sodium chlorid solution when the number of sodium chlorid molecules dissociating in a given time exactly equals the number of undissociated molecules formed in the same time by the union of the sodium and chlorin ions.



220. Chemical Equilibrium. Suppose we examine more carefully the equation representing the reversible reaction,



It is evident that we have four cases of equilibrium between the dissociated and undissociated molecules of potassium nitrate, sodium chlorid, potassium chlorid, and sodium nitrate. Some potassium ions will doubtless unite with chlorid ions to form potassium. In the meantime some of the sodium ions unite with the nitrate ions forming sodium nitrate. This action toward the right side of the equation will continue until it is just offset by the tendency of the ions on the right side of the equation to recombine and form the original substances. Such a solution in equilibrium will contain sodium, potassium, chlorid, and nitrate ions in addition to the undissociated molecules of the four salts.

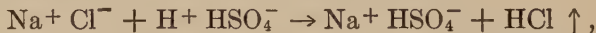
No manufacturing chemist can be very successful by using equilibrium reactions which can never yield 100%. In reality few operations do give a theoretical yield, but the chemist must strive to make his yield as nearly 100% as possible by preventing or destroying the equilibrium of a reaction.

221. Chemical Reactions Run to Completion: (1) *When one of the Products Formed is Insoluble.* In the metathesis reaction to which we referred in section 215,



silver chlorid is *insoluble*. It is precipitated and removed from solution as fast as it is formed. More silver ions combine with more chlorid ions to form more silver chlorid which is also precipitated. Thus the action progresses until all the silver or the chlorid ions are used up. If we start with molar solutions all the ions of both will be used to form silver chlorid. Except for the slight solubility of silver chlorid, less than 2 milligrams per liter, the reaction runs to completion as represented by the arrow in the equation. We may predict that a double decomposition reaction will always occur if one of the compounds that would be formed is insoluble, and that such a reaction will run to completion.

(2) *When One of the Products Formed is Volatile.* If sodium chlorid is heated with sulfuric acid,



we have an *end reaction*, because the product HCl is volatile and escapes as a gas. The hydrogen ion of the sulfuric acid combines with the chlorid ion of the salt to form the gaseous hydrogen chlorid, which is not dissociated. One of the products is being removed as fast as it is formed and there can be no equilibrium. (Note. The backward pressure of the air which tends to prevent the complete removal of the hydrogen chlorid is the only thing that prevents *full* completion of such reactions.) Thus we conclude that *metathesis will occur if one of the compounds that would be formed is volatile; such a reaction runs to completion*. The two facts we have just stated concerning reactions that go to an end are known as Berthollet's laws.

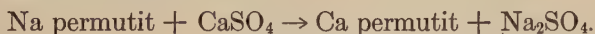
(3) *When One Product Does not Dissociate.* Neutralization reactions between strong bases and strong acids run to completion because water, which does not ionize to a very appreciable extent, is one of the products.



In 10% solutions sodium hydroxid, hydrochloric acid, and sodium chlorid all dissociate to the extent of 50 % or more. Water dissociates to the extent of about 1 part per billion. Thus the above reaction runs practically to completion, the H ion of the acid and the OH ion of the base uniting to form non-ionized water.

222. Mass Action. Some reactions do not *run* to completion, but they may be *driven*. There are several ways in which the direction of a reaction may be changed, or forced to go in the direction desired.

(1) *Effect of an Excess.* If after equilibrium has been reached we increase the *concentration* of one of the factors, the equilibrium is destroyed. This may be done by adding a large excess of one chemical. In our study of softening water, we found that permutit would exchange its sodium for the calcium in the hard water,



But when the permutit has given up all its sodium it may be regenerated by adding a strong (10%) sodium chlorid solution. Thus we increase the *concentration* of sodium ions and by such *mass action* completely reverse the reaction.



Such practice does not differ in principle from the end-reactions previously studied. There we removed one of the products and *prevented* equilibrium. Here we increase the *mass* of one of the factors to *drive* the reaction in the desired direction. Quite often in the laboratory the careless student gets poor results because he argues that if a little is good, more is better. He may change the nature of the reaction entirely by the addition of a large excess of one factor.

(2) *Effect of Temperature.* Temperature plays a very important part in the following reversible reaction,



At a low temperature little nitric oxid is formed, but the yield increases at the high temperature of the electric arc. (See the Birkeland-Eyde process in section 171.)

(3) *Effect of Pressure.* If we heat limestone in a closed tube the reaction will finally come to equilibrium as represented in the equation,

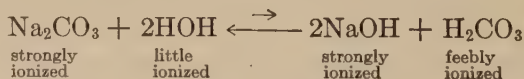


Although a gas, carbon dioxid, is formed, it can not escape and the result is equilibrium. In the commercial method of making calcium oxid (lime) by heating calcium carbonate air is forced through the kiln to sweep away the carbon dioxid and destroy the equilibrium that is otherwise produced by the back pressure of the air (14.7 lb. per sq. in.).

223. Hydrolysis. Although water ionizes very slightly, yet it does dissociate to some extent. When a salt is dissolved in water, enough hydrogen and hydroxyl ions may be formed by this slight dissociation of the water to reverse the ordinary neutralization reaction by which the salt was formed. *Such decomposition of a compound by water is called hydrolysis.*

Sodium chlorid undergoes almost *no* hydrolysis in water since it is the salt of a very strong base and a very strong acid. The degree of ionization of the water is so slight in comparison with that of the acid and base that it is almost negligible.

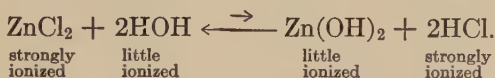
Sodium carbonate hydrolyzes to *some* extent in water solution.



If we study this reaction we see that two of the compounds, sodium carbonate and sodium hydroxid dissociate readily; carbonic acid is a weak acid and dissociates slightly; water is very slightly dissociated. Red litmus dipped into

a sodium carbonate solution is turned blue because the concentration of the *hydroxyl ion* from the very small amount of sodium hydroxid that is formed by hydrolysis is relatively greater than the concentration of the hydrogen ion from the weak carbonic acid. *The salt of a strong base and a weak acid will hydrolyze slightly and its solution will act as a base.* The use of sodium carbonate in washing powders depends upon this fact.

Zinc chlorid is another salt that hydrolyzes *slightly* in water.



In this case the concentration of the *hydrogen ion* from the hydrogen chlorid formed by hydrolysis is much greater than that of the hydroxyl ion from the zinc hydroxid. The solution turns blue litmus red and acts as an acid. The use of this salt in soldering depends upon its ability to act as an acid in water solution and dissolve the oxids of metals. In general, *the salt of a strong acid and a weak base hydrolyzes slightly and its solution acts as an acid.*

Aluminum sulfid hydrolyzes almost *completely* in water.



Both the acid and the base from which the aluminum sulfid is formed are *very weak*. The hydrogen sulfid escapes as a gas and the aluminum hydroxid is precipitated. *The salt of a very weak base and a very weak acid hydrolyzes almost completely.* In all the examples we have studied we find that hydrolysis is just the reverse of neutralization.

SUMMARY

Equilibrium in a chemical reaction is established when the tendency of the factors to combine and form new products is just nullified by the opposing tendency of the products to recombine.

Reactions run to *completion*: (1) *if an insoluble compound is being*

formed; (2) if a volatile product is set free; (3) if a compound is produced that does not ionize.

By changing the concentration of the factors it is possible to force a chemical reaction in the desired direction. This may be accomplished: (1) by use of an excess; (2) by a temperature change; (3) by a change of pressure.

The law of *mass action*, or the law of concentration may be briefly summarized as follows: *The speed of a reaction is proportional to the concentrations of the reacting substances.*

Hydrolysis is the decomposition of a compound, usually a salt, by the action of water. It is the reversal of neutralization.

Almost no hydrolysis occurs when both the acid and the base from which the salt was formed are very strong.

If the acid from which a salt was formed is strong and the base is weak, hydrolysis occurs slightly and the solution acts as an acid. If the base is strong and the acid weak, then the salt will hydrolyze to slight extent and its solution will be basic.

Practically complete hydrolysis occurs when the salt of a very weak base and a very weak acid is added to water.

QUESTIONS

1. Write the equations of Chapter XIV, indicating those that run to completion by a single arrow and those that run to equilibrium by the double arrow. Give the reasons in each case.

2. The first physical chemistry laboratory was opened about forty years ago. Why do you think that all colleges now give courses in physical chemistry?

3. Study the formulas for the following compounds and then tell which ones you would expect to hydrolyze and how its solution would affect litmus; KCl , K_2CO_3 , FeCl_3 , ZnSO_4 , Na_2SO_4 , and AlCl_3 .

4. Would the addition of hydrochloric acid to a solution of zinc chlorid tend to increase or decrease hydrolysis? Explain.

5. Complete each of the following partial equations, indicating whether they run to completion or to equilibrium: (Look up in Table 4 the solubility of the products that you would expect to have formed before you try to write the equation.)

- a. $\text{CuSO}_4 + \text{H}_2\text{S} \rightarrow$
- b. $\text{FeCl}_3 + \text{NaOH} \rightarrow$
- c. $\text{AgNO}_3 + \text{K}_2\text{CrO}_4 \rightarrow$
- d. $\text{BaCl}_2 + \text{NaNO}_3 \rightarrow$
- e. $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4 \rightarrow$

- f. $\text{Fe}(\text{NO}_3)_3 + \text{NaCl} \rightarrow$
- g. $\text{FeS} + \text{H}_2\text{SO}_4 \rightarrow$
- h. $\text{Hg}(\text{NO}_3)_2 + \text{KI} \rightarrow$
- i. $\text{KNO}_3 + \text{ZnCl}_2 \rightarrow$
- j. $\text{AsCl}_3 + \text{H}_2\text{S} \rightarrow$

CHAPTER XXIII

SULFUR AND HYDROGEN SULFID

A. SULFUR

224. Occurrence. Sulfur is very widely distributed, occurring both native, or uncombined, and in such compounds as sulfids and sulfates. Free sulfur is especially common in volcanic regions. Formerly the bulk of the sulfur came from Sicily, but at present Louisiana and Texas are producing enormous quantities.

225. Frasch Process. The sulfur beds in Louisiana lying at a depth of about 500 ft. are in some places 200 ft. thick. Since these beds are covered with quicksand, several attempts to mine the sulfur resulted in failure. Frasch, an American chemist, devised the following successful method of extracting the element. A 12-in. shaft is drilled to the sulfur beds and cased with iron pipe. Inside this casing three concentric pipes, 6 in., 3 in., and 1 in. in diameter respectively, are driven. See Fig. 113. These pipes extend down into the beds of sulfur. Into the outer pipe *superheated water*

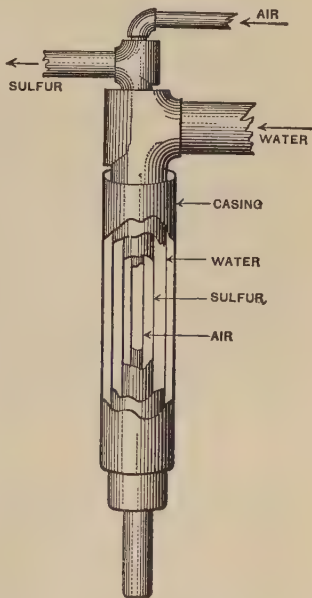


FIG. 113.—Frasch process.

at a pressure of 100 lb. is forced. Under this pressure water can be made hot enough to melt the sulfur. Hot compressed air which is forced down the inner pipe mixes with the melted sulfur and decreases its density enough so it can be easily forced up the middle pipe. See Fig. 114. The molten sulfur flows into wooden bins 20 ft. wide and in some cases 100 ft. long and from 30 to 50 ft. high. When the sulfur solidifies the



FIG. 114.—Stream of molten sulfur issuing from a sulfur well.

sides of the box are removed; the huge block, which may weigh as much as 160,000 tons, is blasted and loaded on cars with steam shovels. See Fig. 115.

226. Purification of Sulfur. The Louisiana sulfur is so pure (99%) that for most purposes it does not require further treatment. Crude sulfur may be purified, however, by distilling it in earthenware retorts. The vapor condenses on the walls and floor of a large brick chamber. The fine powder is called *flowers of sulfur*. The sulfur that con-

denses on the floor of the chamber usually melts and is drawn off into molds to solidify. This product is called *roll sulfur*, or *brimstone*.

227. Physical Properties of Sulfur. Ordinary sulfur is a yellow crystalline solid. It is practically insoluble in water but it dissolves quite readily in carbon disulfid and in the soluble bases. When acids are added to its solution in a

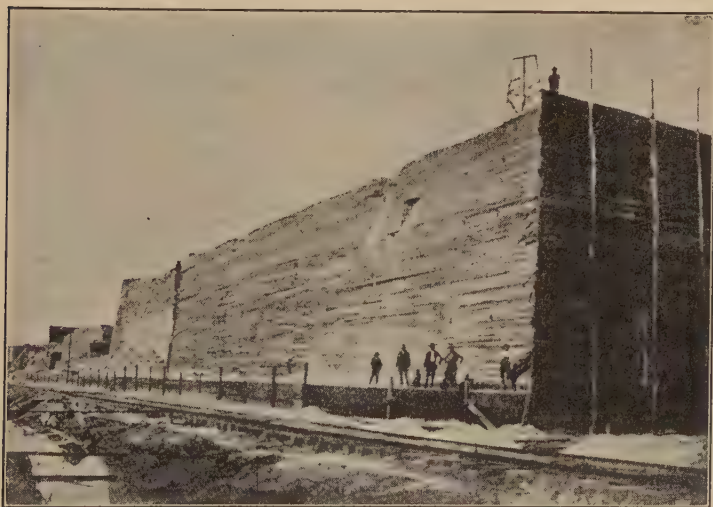


FIG. 115.—A block of Louisiana sulfur. (160,000 tons.)

base the sulfur is precipitated as a fine white powder called *lac sulfur*, or *milk of sulfur*. Ordinary sulfur melts at 114.5° C. forming a pale yellow, mobile liquid. When it is heated still higher, instead of becoming still more mobile as liquids usually do, its viscosity increases. At a temperature of about 250° C. it becomes so thick that it hardly flows from an inverted tube. The color also changes, becoming almost black. When heated still higher, sulfur again becomes more fluid; it boils at 445° C. The physical properties of sulfur are

rather difficult to discuss, since *solid sulfur exists in three different allotropic forms*, each having distinct properties.

(a) *Rhombic Sulfur*. Rhombic sulfur is produced when sulfur crystallizes from solution. Roll sulfur dissolves in

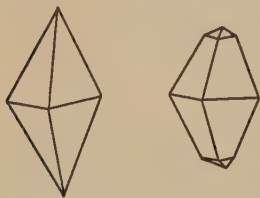


FIG. 116.—Rhombic sulfur crystals.

carbon disulfid readily. As the solution evaporates the sulfur crystallizes in nearly perfect octahedra. See Fig. 116. Rhombic sulfur is stable at the ordinary temperature; its specific weight is a little more than 2.

(b) *Prismatic Sulfur*. Prismatic sulfur is formed when sulfur crystallizes from the molten state. If we melt sulfur in a large crucible, cool it slowly until a crust forms, break the crust and pour off the excess liquid, the interior will contain a mass of pointed needle-like crystals. They belong to the *monoclinic* system of crystallization. See Fig. 117. Monoclinic or prismatic sulfur is soluble in carbon disulfid;



FIG. 117.—Needle-like crystals of prismatic sulfur.

its specific weight is a little less than 2. At temperatures below 96° C. it gradually changes into the rhombic form.

(c) *Amorphous Sulfur*. Non-crystalline sulfur is formed when boiling sulfur is cooled by pouring it into cold water. It is plastic and elastic. Its color is a dark brown. Amorphous sulfur does not dissolve in any ordinary solvent; at

the ordinary temperature it changes slowly into the rhombic modification. Thus we see that the stability of the different allotropic forms of sulfur depends upon the temperature. See Fig. 118.

228. Chemical Properties.

At the ordinary temperature sulfur is quite inactive. At higher temperatures it is quite as active as oxygen. It unites with oxygen forming sulfur dioxide.

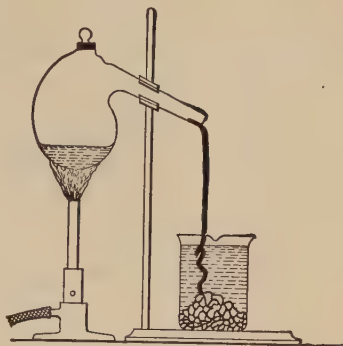


FIG. 118.—Amorphous sulfur.

When metals are heated with sulfur the union of the two elements is so energetic that heat and light are evolved. The product formed is a *sulfid*. Compounds of sulfur and the non-metals are not formed so readily, and they are quite unstable. Chemically sulfur behaves in a manner analogous to oxygen. The following list of compounds shows the similarity between the compounds of sulfur and those of oxygen. If the oxid of a metal is insoluble, generally the sulfid of the same metal is insoluble.

Hydrogen sulfid. H_2S	Hydrogen oxid. H_2O
Copper sulfid. CuS	Copper oxid. CuO
Zinc sulfid. ZnS	Zinc oxid. ZnO
Magnesium sulfid. . MgS	Magnesium oxid. . . . MgO

229. Uses of Sulfur. Sulfur is used in making sulfur dioxide, carbon disulfid, and other compounds of sulfur. Large quantities are burned for use in preparing sulfuric acid. Matches, fireworks, and black gunpowder all contain sulfur or sulfur compounds. Large quantities of sulfur are now used in preparing sulfur dyes, especially for making the fast blacks used for dyeing hosiery.

When sulfur is mixed with rubber and heated moderately for several hours *vulcanized* rubber is formed. The product is elastic and impervious. Its hardness depends upon the relative amount of sulfur used and the heat applied. The soft rubber used for waterproofing materials, for rubber tubing and for rubber stoppers contains only a small percentage of sulfur. For automobile tires a larger quantity is used; ebonite is a black variety of hard rubber used for insulating material.

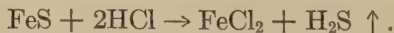
Sulfur is boiled with lime and water to prepare *lime sulfur* spray which finds extensive use in killing insects and fungi that damage fruit trees.

B. HYDROGEN SULFID

230. Occurrence. All protein material contains a certain amount of sulfur. When such protein decays small quantities of hydrogen sulfid are formed. Traces of hydrogen sulfid get into the air from the burning of coal, since coal is seldom free from sulfur. The tarnishing of silverware and certain metals is caused by the action of hydrogen sulfid in forming metallic sulfids.

231. Preparation. Although hydrogen combines directly with molten sulfur to form hydrogen sulfid yet this method of preparing the gas is not practical since the action is reversible.

Hydrogen sulfid is generally prepared by the action of an acid on the sulfid of a metal. Iron sulfid and hydrochloric acid interact as represented by the following equation:



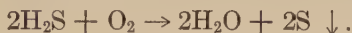
232. Physical Properties. Hydrogen sulfid is a colorless gas; it has a disagreeable odor resembling rotten eggs. It is heavier than air and moderately soluble in water. The gas is poisonous when inhaled, small quantities producing nausea, headache, and dizziness.

233. Properties, Chemical. The chemical properties of hydrogen sulfid are quite important; they may be grouped as follows:

1. *Hydrogen Sulfid Burns.* When the supply of air or oxygen is sufficient for complete oxidation, the hydrogen is oxidized to water and the sulfur to sulfur dioxide.



In an insufficient supply of air hydrogen sulfid burns forming water and free sulfur.



It is also possible to have just enough oxygen to form a mixture of water, sulfur dioxide, and sulfur. When a solution of hydrogen sulfid is exposed to the air slow oxidation occurs, sulfur being precipitated.

2. *Hydrogen Sulfid a Reducing Agent.* Since hydrogen sulfid decomposes easily into hydrogen and sulfur, it is a good reducing agent, for sulfur and hydrogen both have a strong affinity for oxygen. If the gas is passed through a solution of hydrogen peroxid, it reduces the peroxid to water. At the same time the hydrogen of the gas is oxidized. Sulfur is precipitated in the form of a fine white powder.

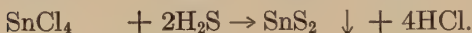
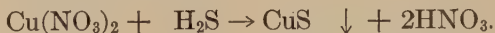


3. *Hydrogen Sulfid an Acid.* In water solution the gas turns blue litmus red, neutralizes bases, and behaves in other ways like a *weak* acid. Its water solution is often called *hydrosulfuric acid*.

4. *Hydrogen Sulfid Acts on Metals.* The water solution of hydrogen sulfid acts on metals forming sulfids. Organic substances, especially eggs, mustard, etc., contain considerable sulfur. As they decay hydrogen sulfid is formed. A silver spoon left in contact with such foods soon becomes

covered with a coating of silver sulfid. The tarnishing of some other metals is due to the formation of a sulfid.

234. Uses. The most important use of hydrogen sulfid is as a reagent in qualitative analysis. Nearly all metallic sulfids are insoluble in water. If we add hydrogen sulfid to solutions of the salts of metals the insoluble sulfids will be thrown out of solution as precipitates. The following equations are typical examples:



When hydrogen sulfid is added to a solution containing a number of different metallic salts, sulfids of all the metals are precipitated together. In *qualitative analysis* the student learns how to separate these sulfids and identify each. For example, the sulfids of zinc and manganese are soluble in dilute acids; arsenic sulfid and tin sulfid are soluble in ammonium sulfid; the sulfids of copper and lead are soluble in hot nitric acid while mercuric sulfid is insoluble. Carefully worked out schemes of analysis are based to a large extent upon the solubilities of the sulfids of metals in different reagents.

235. Sulfur Springs. Hydrogen sulfid is found in certain natural springs and in artesian waters. It imparts a disagreeable odor to the water and a peculiar taste. As oxidation occurs when the water comes into contact with the air the sulfur is deposited. Some sulfur springs are supposed to have certain medicinal properties.

236. Carbon Disulfid. Carbon disulfid, CS_2 , is a compound prepared by the action of sulfur vapor on charcoal in an electric furnace. It is a heavy oily liquid; nearly colorless. The commercial product has a very disagreeable odor. It is not miscible with water. Its vapor is very in-

flammable, the products of combustion being sulfur dioxide and carbon dioxide.



It is used as a solvent for sulfur, phosphorus, waxes, and resins. A solution of rubber in carbon disulfide is used as rubber cement. Carbon disulfide is used quite extensively for destroying insects and other small animals, since its vapor is poisonous and the products of its combustion are suffocating. When carbon disulfide is poured into the burrows of gophers and other small animals and then ignited, the heavy products of combustion soon settle down to the animals underground.

SUMMARY

Sulfur occurs in volcanic regions. It is believed that beds of sulfur are sometimes formed by the decomposition of sulfates in the presence of bacteria. Rich deposits of sulfur are found in Louisiana and Texas.

Crude sulfur is purified by *distillation*. It is sold as *flowers of sulfur*, *roll sulfur*, and *lac sulfur*.

Sulfur exists in three solid allotropic forms: *rhombic* sulfur, *prismatic* sulfur, and *amorphous* sulfur. Sulfur is about twice as heavy as water; it is insoluble in water but dissolves readily in carbon disulfide.

Sulfur burns with a pale blue flame forming sulfur dioxide. It unites readily at higher temperatures with most metals.

Hydrogen sulfide is prepared by the action of an acid on a sulfide. It is a colorless gas with a very disagreeable odor. The gas is heavier than air and soluble in water.

Hydrogen sulfide burns with a blue flame. It is a reducing agent. *In water solution it acts like an acid* and it combines with metals to form sulfides. It is used in qualitative analysis.

Carbon disulfide is an oily liquid; it burns readily. It is used as a solvent, and as a germicide and insecticide.

QUESTIONS

1. Write three equations for the burning of hydrogen sulfide, varying the amount of oxygen used.

2. Devise a method of testing for traces of hydrogen sulfide.

3. Why does silverware tarnish so readily in city dwellings?
4. Lead sulfid is black. Would you recommend the use of white lead for painting the walls and ceiling of a chemical laboratory? Explain.
5. Write the equations to show the reaction of hydrogen sulfid with the chlorids of mercury, antimony, zinc, nickel, and bismuth. In which one of these reactions will no precipitate be formed, and why?
6. How do you account for the unpleasant odor and taste of certain springs?
7. Why does a rubber band stretched over a silver coin soon form a brown mark or stain?
8. Why do we call a solution of hydrogen sulfid a weak acid? Do you think such a solution would be a good conductor?
9. Write equations to show three methods of preparing copper sulfid.
10. Why can not you use nitric acid for preparing hydrogen sulfid?

PROBLEMS

1. Compute the weight of one liter of hydrogen sulfid.
2. How many grams of iron sulfid must be used to prepare 100 liters of hydrogen sulfid?
3. How many pounds of sulfur must be used to make 400 lb. of copper sulfid, CuS ?
4. How many liters of air must be used to burn completely 40 liters of hydrogen sulfid?

CHAPTER XXIV

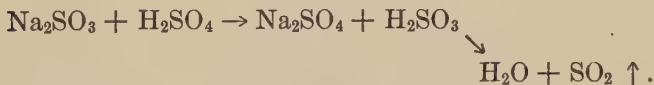
OXIDS AND ACIDS OF SULFUR

A. SULFUR DIOXID

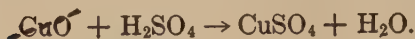
237. Occurrence. Since coal usually contains sulfur, some sulfur dioxid finds its way into the air when coal is burned. Many sulfids are found in nature, those of copper, lead, and zinc for example. Before these metals are extracted from their ores, they are roasted (heated in air) to convert them into oxids. In this way tons of sulfur dioxid escape from the stacks of smelters.

238. Preparation. 1. *Burning Sulfur.* When sulfur is burned in air, sulfur dioxid, SO_2 , is formed. Since the product mixes with the nitrogen and other gases from the air, this method is not a practical one if reasonably pure sulfur dioxid is desired.

2. *Decomposition of Sulfites.* Sulfur dioxid is frequently prepared by the action of an acid on a sulfite. If sodium sulfite and sulfuric acid are used the products formed are water, sulfur dioxid, and sodium sulfate.



3. *Reduction of Sulfuric Acid.* Hot concentrated sulfuric acid acts as an oxidizing agent in the presence of certain metals. A part of the sulfuric acid is thus decomposed with the liberation of sulfur dioxid. The reaction is complex, but it is probable that a series of reactions may occur about as follows:



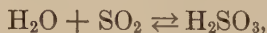
If we cancel the factors and products that are common to both sides of the equation, we may then combine the *partial* equations into the following *final* equation:



239. Physical Properties. Sulfur dioxid is a colorless gas with a choking odor. As prepared in the laboratory it is usually whitish in appearance due to the presence of finely divided particles of sulfur trioxid. Sulfur dioxid is more than twice as heavy as air; it is very soluble in water. It is one of the easiest gases to liquefy, and liquid sulfur dioxid is put on the market in metal containers.

240. Chemical Properties. 1. *Activity.* Sulfur dioxid does not burn although it may be oxidized to sulfur trioxid, SO_3 , by using suitable catalysts. Thus it may act as a *reducing* agent. Sulfur dioxid is quite a stable compound; hence it does not support combustion.

2. *Acid Action of Sulfur Dioxid in Solution.* Sulfur dioxid is the anhydrid of *sulfurous acid*. The solution of this gas in water,



is a weak acid, turning blue litmus red, and neutralizing bases forming *sulfites*. Sulfurous acid is unstable and readily breaks up into water and sulfur dioxid. It may combine with oxygen from the air to form sulfuric acid.

3. *Bleaching Action.* Sulfur dioxid unites with the colored compounds of many organic substances forming colorless compounds. For example, sulfur dioxid unites with the natural yellow color of straw to form a colorless compound.

The substance to be bleached must be moist. Some chemists believe that the bleaching action of sulfur dioxide in solution is sometimes due to its ability to act as a reducing agent.

241. Uses of Sulfur Dioxid. Sulfur dioxide is used as a disinfectant and insecticide. It prevents the growth of yeasts, molds, and bacteria. Hence it is sometimes used as a preservative in such food-stuffs as canned corn, sausage, and fruits. Since it is injurious to higher forms of life as

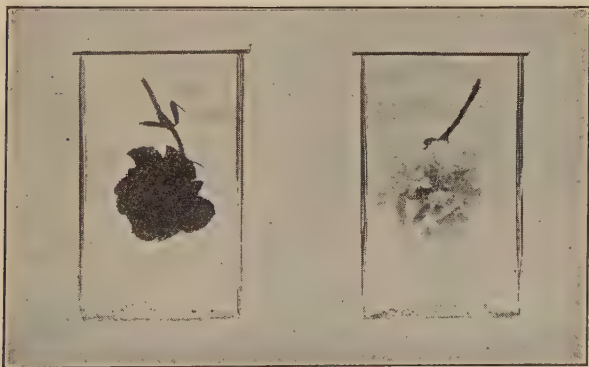


FIG. 119.—Carnations showing the bleaching effects of sulfur dioxide.

well as to lower animal and plant life, its use as a preservative is questionable.

Considerable sulfur dioxide is used to bleach wool, silk, and straw. The colorless compound that is formed by the union of the dioxide with the natural color is unstable; it decomposes in sunlight giving the original color. Certain food-products, such as molasses and dried fruits are often bleached by sulfur dioxide. A moist carnation put into a bottle of sulfur dioxide soon loses its color. See Fig. 119. Maraschino cherries are bleached by sulfur dioxide and then dyed a bright red or green color. Sulfur dioxide is used in some of the "iceless" refrigerators. A small electric motor

operates a compressor that is used to liquefy the sulfur dioxid. The refrigerator in which such a compressor is

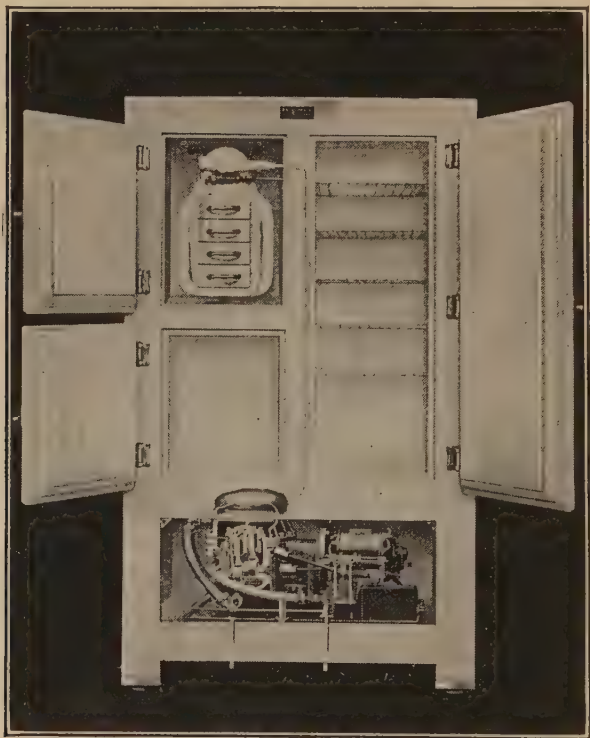


FIG. 120.—Sulfur dioxid is liquefied in the lower compartment. As it evaporates in the coils (upper left) it absorbs heat and freezes water in the shallow pans.

installed is kept cool by the evaporation and expansion of the sulfur dioxid. See Fig. 120.

Large quantities of sulfur dioxid are used in the preparation of sulfites, but its most important use is in manufacturing sulfuric acid.

242. Sulfitcs. A few of the sulfitcs arc important compounds. The sulfitcs and bi-sulfitcs of sodium and potassium arc soluble salts. *Calcium bi-sulfite*, $\text{Ca}(\text{HSO}_3)_2$, is extensively used in making wood pulp in the paper industry.

B. SULFUR TRIOXID AND SULFURIC ACID

243. Sulfur Trioxid. Sulfur trioxid is the anhydrid of sulfuric acid. At the ordinary temperature it is a colorless liquid. In the presence of a trace of moisture sulfur trioxid forms a white solid which dissolves in water with a hissing sound. This anhydrid is a vigorous oxidizing agent. Sulfur trioxid is one of the intermediate products formed in the manufacture of sulfuric acid.

244. Manufacture of Sulfuric Acid. Two methods of making sulfuric acid arc used extensively. Both depend upon the fact that sulfur dioxid may be oxidized indirectly to form the sulfur trioxid, which combines with water.



In the contact process the sulfur dioxid is oxidized by means of a catalyst, while in the chamber process nitric oxid is used to take oxygen from the air and "carry" it to the sulfur dioxid.

1. *Contact Process.* When sulfur dioxid is heated with air sulfur trioxid forms very slowly. In the presence of a suitable catalyst, such as ferric oxid or finely divided platinum, the union of the oxygen with the sulfur dioxid occurs rapidly enough so that the method may be used commercially.

The sulfur dioxid, obtained by roasting iron pyrites, FeS_2 , is mixed with air and passed through heated iron pipes containing the contact agent. It was found that impurities such as arsenic, which is usually found with iron pyrites, rapidly "poison" the catalyst so that it soon ceases to work. Therefore the raw material must be carefully purified before it

reaches the contact agent. The absorption of the sulfur trioxid was another difficulty in this process. While a lump of the trioxid will unite with water readily, the finely divided material will bubble successively through several jars of water with little absorption. Therefore the trioxid that is formed in this process is absorbed in very concentrated sulfuric acid and then diluted to the desired strength.



The contact process is used to some extent in America, but more extensively in Europe. It yields a high-grade product of a high degree of concentration.

2. *Chamber Process.* In the chamber process sulfur dioxide is oxidized to the trioxid by the use of oxids of nitrogen; the sulfur trioxid combines with water to form sulfuric acid. We have seen that nitric oxid acts as a carrier of oxygen, taking it from the air and giving it up to a reducing agent such as sulfur dioxide. (See section 178.) The nitric oxid is not wasted after it has carried a supply of oxygen, but it is used again and again. See Fig. 121.

In practice the sulfur dioxide, formed by burning sulfur or roasting iron pyrites, FeS_2 , together with oxids of nitrogen and an excess of air, is conducted from the burners *B* into the Glover tower. As the gases ascend through the tower, which is filled with lumps of quartz, or some acid-resisting brick, they meet two streams of sulfuric acid. One of these streams of acid is concentrated; it comes from the Gay-Lussac tower and contains dissolved oxids of nitrogen, which are set free in the Glover tower and enter the first chamber with the sulfur dioxide, air, and steam. The other stream of sulfuric acid is more dilute. It becomes more concentrated in the Glover tower and flows down to the bottom into the acid egg *E* from which it is forced by compressed air up to the top of the Gay-Lussac tower to be used for re-dissolving the oxids of nitrogen which are to be used over and over again.

The main chemical reactions occur in lead chambers, which may be 100 ft. long, 40 ft. high and 20 ft. wide. Four of these chambers

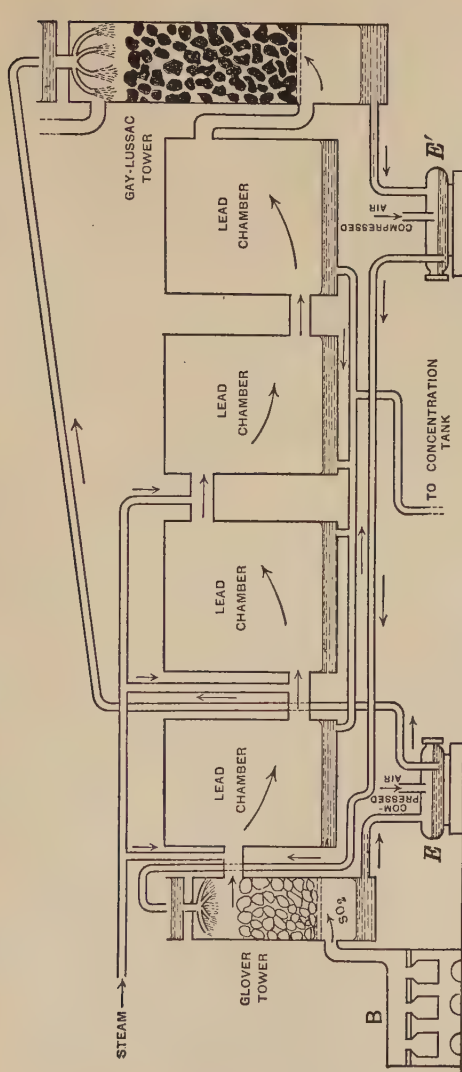


FIG. 121.—Diagram to illustrate the chamber process of making sulfuric acid.

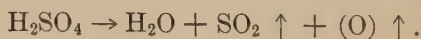
are generally used in a single plant. The reactions are complicated, but the steam, sulfur dioxid, air, and nitric oxid all interact to form dilute sulfuric acid which collects in the lead chambers. Sulfuric acid does not act on lead until it is fairly concentrated, nearly 80%. For many industrial purposes the acid does not need further concentration. If a more concentrated acid is desired, further concentration is carried on in glass or platinum vessels. As the concentration of this acid is the most costly part of the process, the bulk of the concentrated acid of commerce is now made by the contact process.

Some of the oxids of nitrogen from the last chamber are absorbed in the Gay-Lussac tower by concentrated acid from the Glover tower which trickles down over layers of coke. This "nitrose" acid flows into the egg *E'* from which it is forced to the top of the Glover tower to be used over again. Waste gases, including nitrogen and some of the lower oxids of nitrogen, pass out through a stack at the top of the Gay-Lussac tower.

245. Physical Properties. Sulfuric acid is a heavy, oily liquid; it is frequently called "oil of vitriol." Ordinary concentrated sulfuric contains about 93.5% acid; its specific weight is from 1.83 to 1.84. The boiling point of this acid is higher than that of most common acids, about 338° C. Pure sulfuric acid is colorless but the commercial acid is often colored yellow to almost black due to impurities, especially organic matter. When sulfuric acid is added to water, a great deal of heat is evolved. The action is chemical, since hydrates of sulfuric acid, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, are formed. These hydrates decompose when the acid solution is heated.

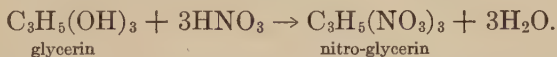
246. Chemical Properties. 1. *Acid Action.* Dilute sulfuric acid has all the properties that are characteristic of typical acids. It acts on metals, the oxids of metals, and neutralizes bases forming *sulfates*.

2. *As an Oxidizing Agent.* When sulfuric acid is heated it decomposes into water, sulfur dioxid, and oxygen.



The nascent oxygen is a vigorous oxidizing agent. Thus *hot concentrated* sulfuric acid acts as an oxidizing agent exactly analogous to hot nitric acid, although it is not so vigorous in its action. The action of hot sulfuric acid as given in section 238 is typical of the behavior of this acid with metals. The *cold, dilute* acid interacts with some metals liberating hydrogen.

3. *As a Dehydrating Agent.* Sulfuric acid has a strong affinity for water. Gases are often dried by bubbling them through the acid. Not only does sulfuric acid absorb water, but it takes hydrogen and oxygen from many organic compounds and leaves carbon as a residue. In this manner sulfuric acid chars wood, paper, cotton, sugar, and other organic matter. The hot concentrated sulfuric acid will also completely oxidize the carbon, if the heating is continued. In making explosives the action of nitric acid on the organic matter forms water. For example,



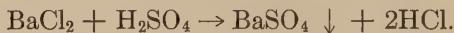
In such reactions sulfuric acid is always mixed with the nitric acid to absorb the water as fast as it is formed and thus prevent the dilution of the nitric acid.

247. Uses. To mention all the uses of sulfuric acid would require a long chapter, and it would necessitate naming nearly all the industries. So general is the use of this chemical that the following statement is often made: "The civilization of a country is measured by the amount of sulfuric acid it uses." Several million tons are made annually in the United States. In the explosives industry large quantities are used. Still larger quantities are used in making commercial fertilizers. In refining petroleum sulfuric acid is used to char certain organic impurities. In cleaning metals, making sulfates, and in the preparation of acids large quantities of this acid are used. From the preceding paragraphs

we find that this acid is used quite extensively in its own preparation. It is not astonishing that Ellwood Hendrick calls sulfuric acid the "old horse" of chemical industry.

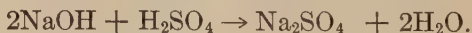
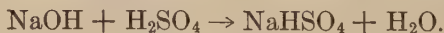
248. Sulfates. The sulfates form a very important class of salts. Since sulfuric acid used to be known as "oil of vitriol," these salts are popularly known as vitriols. Copper sulfate is commonly called blue vitriol; zinc sulfate, white vitriol; and ferrous sulfate, green vitriol. Nearly all sulfates are soluble, the sulfates of lead, calcium, barium, and strontium being the chief exceptions.

249. Test for a Sulfate. When a solution of barium chlorid is added to a solution containing sulfuric acid, or any soluble sulfate, a white precipitate of barium sulfate is formed.



This precipitate is insoluble in hydrochloric acid. Therefore in testing a solution to see whether it contains a sulfate, we first add a little hydrochloric acid and then a solution of barium chlorid. If a white precipitate forms, we know that the solution contained a sulfate.

250. Sulfuric Acid May Form Two Kinds of Salts. When we studied the ionization of acids, we learned that sulfuric acid may ionize to produce the HSO_4^- ion, or more completely to form the $\text{SO}_4^{=}$ ion. As a result it may interact with metals or bases to form salts having either ion. For example,



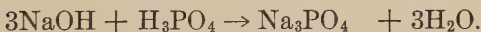
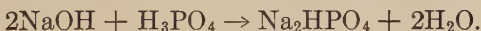
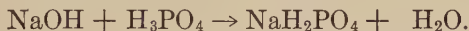
In the first case one atom of sodium replaces just one of the two hydrogen atoms of sulfuric acid and forms *sodium acid sulfate*, NaHSO_4 . An *acid salt* always contains some of the hydrogen of the acid from which it was formed. Sodium acid sulfate is often called sodium *bi-sulfate*. An *acid like sulfuric that has two replaceable hydrogen atoms per molecule is called a di-basic acid*. From the second equation we see that one mole

of such an acid just neutralizes two moles of a base like sodium hydroxid. Thus the name *di-basic*.

From a study of the second equation, we see that complete neutralization of the sulfuric acid forms sodium sulfate, Na_2SO_4 , a *normal* salt. Such salts are often called *neutral* salts, an unfortunate name since many of them act as acids or bases in solution. (See hydrolysis, section 223.)

A glance at the formulas for nitric acid and hydrochloric acid must convince us that they can form *normal salts only*, since they have only one hydrogen atom per molecule. Such acids are *mono-basic*. It is obvious that sulfuric acid can form just twice as many salts as either one of these acids.

Phosphoric acid, H_3PO_4 , is a *tri-basic* acid; it has three *replaceable* hydrogen atoms in its molecule. It may form three different salts as represented by the following equations:



In the first case we have formed NaH_2PO_4 , which is called *mono-sodium phosphate*, or *di-acid sodium phosphate*; the salt Na_2HPO_4 is called *di-sodium phosphate*, or *acid sodium phosphate*; the third salt, Na_3PO_4 , is *tri-sodium phosphate*, or *normal sodium phosphate*.

251. Other Acids of Sulfur. A large number of acids of sulfur are known. With the exception of those already discussed, few are very important. *Hypo-sulfurous acid* probably has the formula $\text{H}_2\text{S}_2\text{O}_4$. *Per-sulfuric acid*, $\text{H}_2\text{S}_2\text{O}_8$, is a very vigorous oxidizing agent. *Pyro-sulfuric acid*, or *fuming sulfuric acid*, has the formula $\text{H}_2\text{S}_2\text{O}_7$. It finds use in the dye industry. Under the name *oleum* large quantities of this acid were used during the World War for making "smoke screens." Salts of the unstable *thio-sulfuric acid*,

$\text{H}_2\text{S}_2\text{O}_3$, are known. The sodium salt is extensively used in photography under the common name of "hypo."

SUMMARY

Sulfur dioxid is formed: (1) *by burning sulfur*; (2) *by roasting sulfids*; (3) *by decomposing sulfuric acid*; and (4) *by the action of an acid on a sulfite*.

Sulfur dioxid is a heavy suffocating gas; it is very soluble in water; sulfur dioxid is very easy to liquefy.

Chemically sulfur dioxid is a *reducing* agent; its water solution has all the properties of a weak acid. Sulfur dioxid is a good disinfectant and antiseptic.

Sulfur dioxid is used as a germicide, a preservative, a bleaching agent, and in the preparation of sulfites and sulfuric acid.

Sulfur trioxid is prepared by oxidizing sulfur dioxid by the use of a suitable catalytic agent. Sulfur trioxid is the anhydrid of sulfuric acid.

Sulfuric acid may be made by the *contact* process or the *chamber* process. It is a heavy oily liquid that mixes with water in all proportions. Chemically sulfuric acid *acts as an acid* when dilute; it acts as an *oxidizing agent* when concentrated and also as a *dehydrating agent*.

Sulfuric acid is used in nearly all industries.

A di-basic acid has two replaceable hydrogen atoms per molecule; it forms two classes of salts: *acid salts*, and *normal salts*.

QUESTIONS

1. State three reasons why sulfuric acid is used in preparing other acids.
2. How would you prepare pure sulfur dioxid? Can this gas be collected by water displacement?
3. In diluting sulfuric acid, why should the acid be poured into the water?
4. Would it be possible for sulfuric acid to form an acid salt with calcium hydroxid? If so, write the equation.
5. Cream of tartar is a salt. How do you account for its sour taste and its action as an acid in baking powders?
6. How many sodium salts could be formed with a tetra-basic acid?
7. How would you test a solution to see whether it contains a sulfate?

8. How could you test a solution to see whether it contains a sulfite?

9. Why do straw hats become yellow so quickly when exposed to sunlight? Newspapers also become "yellow with age." Explain.

10. One often finds a brown ring on a table or wooden shelf where a bottle of sulfuric acid has been standing. Explain.

11. Of what value is a beaker partially full of sulfuric acid in the glass case of a chemical balance?

12. Why does boiling sulfuric acid produce such frightful burns?

PROBLEMS

1. How many pounds of sulfuric acid can be prepared from one ton of sulfur that is 98% pure?

2. Calculate the weight of one liter of sulfur dioxide. Compare the weight of sulfur dioxide with that of air.

3. How many liters of sulfur dioxide will be formed by the action of an excess of sulfuric acid on 120 gm. of sodium sulfite?

4. How many pounds of ferrous sulfate can be made by the action of sulfuric acid on 400 lb. of iron?

CHAPTER XXV

THE HALOGEN FAMILY

252. The Halogen Family. The four elements, fluorin, chlorin, bromin, and iodine, are known as halogens. The word *halogen* means salt-producer. These elements are very similar in their chemical behavior, and for that reason they are usually studied together as a family, or group. In most of their compounds, these elements act negatively and have a

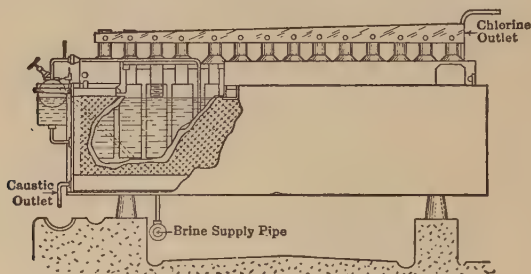


FIG. 122.—Sectional diagram of the Nelson cell.

valence of one. As a positive element some of them may have a valence as high as seven.

A. CHLORIN

253. Occurrence. Since chlorine is a very active element, it never occurs free in nature. It is found in chlorides, especially those of sodium and potassium. Magnesium chloride is also fairly abundant. These chlorides are all found in seawater and in certain localities as alkaline deposits.

254. Preparation. 1. *By Electrolysis (Commercial).* Chlorine is prepared on a large scale by the electrolysis of a

solution of sodium chlorid. The chlorin is set free at the anode, and the sodium at the cathode where it attacks water and forms sodium hydroxid and hydrogen. The by-product is sodium hydroxid. To keep the chlorin from coming into contact with the hydrogen or the sodium hydroxid, a diaphragm is used.

In the Nelson cell, Fig. 122, a narrow steel tank contains the electrolyte. A perforated, U-shaped piece of sheet iron

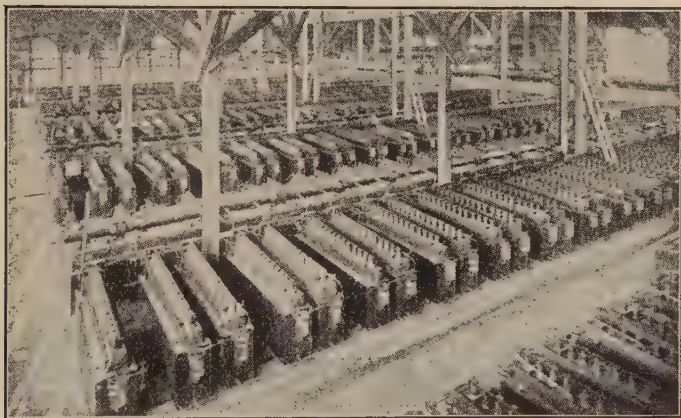


FIG. 123.—One of the eight cell-rooms of the Edgewood Arsenal.

serves as the cathode. Graphite rods which are immersed in the brine serve as the anodes. A closely woven asbestos diaphragm, supported by the cathode, is used to keep the chlorin from reuniting with the sodium of the sodium hydroxid.

Fig. 123 shows one of the eight cell rooms at the Edgewood Arsenal. This plant, which was built by the United States in 1917-8 had a capacity of 100 tons of chlorin per day. This was the largest chlorin plant ever built and the greatest electrolytic installation known.

2. *Oxidation of Hydrogen Chlorid (Laboratory Method).* In

the laboratory chlorin is often prepared by heating hydrogen chlorid with an oxidizing agent such as manganese dioxid, MnO_2 .



The hydrogen of the acid is oxidized to water. If any tetra-chlorid of manganese, MnCl_4 , is formed at all, it immediately decomposes to form manganous chlorid, MnCl_2 , and chlorin. The change of valence of the manganese from four to two is interesting.

Since hydrogen chlorid is formed by the action of sulfuric acid on sodium chlorid, chlorin may be prepared by adding an oxidizing agent to a mixture of these compounds. The equation follows:



255. Physical Properties. Chlorin is a greenish-yellow gas about $2\frac{1}{2}$ times as heavy as air; it has a very disagreeable suffocating odor. When inhaled in small quantities it attacks the mucous membrane of the nose and throat producing the same effect as a heavy cold. In larger quantities it produces death. The effects from breathing chlorin are partially alleviated by inhaling alcohol or ammonia. Chlorin is fairly soluble in water, imparting to the solution a pale yellow color.

256. Chemical Properties. 1. *Action with Metals.* If we sprinkle powdered antimony into a jar of chlorin, the two elements combine spontaneously to form antimony tri-chlorid. The action is so energetic that heat and light are evolved. Other metals, such as copper, zinc, iron, and arsenic, also combine directly with chlorin, especially if heated slightly.

2. *Action with Hydrogen.* A mixture of hydrogen and chlorin in direct sunlight explodes violently. These ele-

ments combine more slowly in diffused daylight. Chlorin does not support ordinary combustion, but if a candle is lighted and thrust into a jar of chlorin it continues to burn emitting a smoky flame. The hydrogen of the candle wax unites with the chlorin to form hydrogen chlorid and the carbon is set free. If a strip of filter paper is moistened with warm turpentine and suspended in chlorin, it bursts into flame, hydrogen chlorid being formed and the carbon of the turpentine liberated as a dense black soot. Thus we see that *chlorin not only combines directly with hydrogen to form hydrogen chlorid but it has the ability to abstract hydrogen from compounds.*

3. *Action with Water.* When chlorin water stands in sunlight the chlorin *gradually* takes the hydrogen from the water to form hydrogen chlorid and oxygen is liberated.



The nascent oxygen which is liberated by this decomposition of the water attacks coloring matter oxidizing it to form colorless compounds. Thus chlorin acts as a *bleaching agent*. Since a substance must be wet to be bleached by chlorin it is quite evident that the bleaching action depends upon the nascent oxygen and is an oxidizing process. In the laboratory *chlorin water* is sometimes used as an oxidizing agent. Some dyes are not affected by chlorin but the natural yellow color of fibers is readily destroyed. See Fig. 124.

257. Uses of Chlorin. 1. *As a Bleaching Agent.* For use in bleaching, chlorin is usually obtained from *bleaching powder* or *chlorid of lime*. This compound is prepared by passing chlorin gas into calcium hydroxid.



No definite formula can be given to this compound but it appears to be a salt of hydrochloric and hypochlorous acids

closely corresponding to the formula CaOCl_2 . Chlorin is easily liquefied and is sometimes transported in metal cylinders. In a new bleaching process an electric current is passed through a solution of sodium chlorid. The article to be bleached is attached to the anode. Students sometimes get the idea that chlorin will bleach any substance. Many colors are not affected by chlorin at all. While the color of ordinary ink is usually destroyed by chlorin, printer's ink is not affected at all. Ink eradicators generally contain

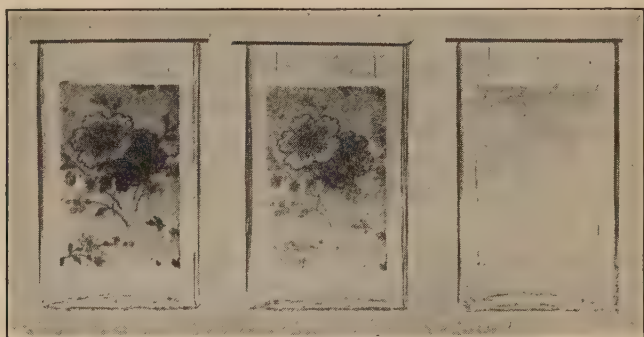


FIG. 124.—Bleaching effect of chlorin.

citric or tartaric acid (solution 1) and some hypochlorite (solution 2). When the two solutions mix, hypochlorous acid is set free.

For removing stains or spots on linen or cotton, Labarraque's solution is used. This is made by mixing a solution of sodium carbonate with a solution of calcium hypochlorite obtained by boiling water and bleaching powder. This solution must never be used with wool or silk, nor with any colored prints. This solution is often incorrectly called Javelle water. There is little difference in the behavior of the two solutions, but Javelle water contains potassium hypochlorite instead of sodium hypochlorite.

Fig. 125 shows a common method used in bleaching cotton

goods. To remove the wax from fibers that are to be bleached, a preliminary treatment is necessary. This consists in boiling the cloth with very dilute caustic soda or with sodium carbonate. From the roll, *R*, the goods are drawn through a vat, *b*, containing bleaching powder and water; they then go into a sulfuric acid vat, *a*, where hypochlorous acid,

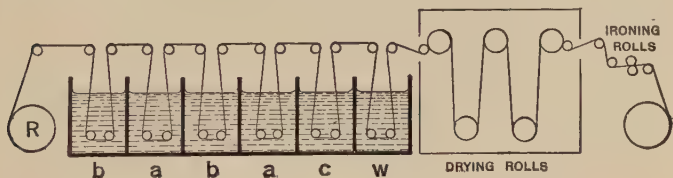


FIG. 125.—Commercial method of bleaching cotton goods.

HClO , is liberated by the action of the acid on the bleaching powder, as in the following equation:



As the HClO decomposes nascent oxygen is set free, acting as the bleaching agent. The cotton strip then passes through a second vat containing bleaching powder and then a second acid vat. Since any excess chlorin slowly destroys the fiber, an *antichlor* is used in vat *c* to remove the last traces of chlorin. The strip is then washed, ironed, and re-rolled.

2. As a *Disinfectant*. Since moist chlorin is a good oxidizing agent in the presence of organic matter, bacteria are readily destroyed by it. Large quantities of "chlorid of lime" are used as a disinfectant. Large quantities of liquid chlorin are used for purifying city water supplies. Many municipalities and amusement parks have built swimming pools. The water in such pools is often treated with chlorin for purification.

When the influenza epidemic took so many lives during the late war, it was noticed that the men who were working

with chlorin in the preparation of poisonous gases seemed to be more or less immune from this dread disease. The War Department has continued to do research work with chlorin as a disease preventive. It appears that as small an amount as one part of chlorin in 100,000 parts of air not only serves as an aid in preventing influenza, but that it is also quite successful in curing colds. Therefore clinics are now being opened for administering chlorin.

3. *For Chlorin Compounds.* Large quantities of chlorin are used in making chlorin compounds. Chloroform contains a large percentage of chlorin. Carbon tetrachlorid, another chlorin compound, is extensively used as a cleansing agent and as a fire extinguisher. Chlorin was made on a very large scale during the war because practically all the poison gases used at that time were compounds containing this element.

4. *Chlorin in Warfare.* April 22, 1915, the Germans released great clouds of chlorin from rows of cylinders that had been secreted in the trenches. This heavy gas was carried by the winds to the Canadians occupying the Ypres salient. Since the men were without masks, the casualties were heavy. Within a week, however, the women in France and England made over 2,000,000 small bags and filled them with "hypo" crystals. These crude masks, when tied over the nose and mouth of a soldier, made him temporarily immune to chlorin attacks. Much more efficient gas masks were prepared later to nullify the effects of such poisonous gases as chlorpicrin, mustard gas, and phosgene, all chlorin compounds which will be discussed more fully in a later chapter.

B. HYDROGEN CHLORID

258. Preparation. Commercially hydrogen chlorid is prepared by the same method as that used in the laboratory, heating sodium chlorid with sulfuric acid.



The gas is collected in the laboratory by air displacement. In the commercial preparation, the gas is dissolved in pure water and marketed as *hydrochloric*, or *muriatic* acid.

259. Physical Properties. Hydrogen chlorid is a colorless gas with a sharp, penetrating odor. It is heavier than air and dissolves readily in water. One volume of water at standard conditions will absorb a little more than 500 volumes of this gas. The gas *fumes* strongly in moist air, because it is so readily soluble that it takes water from the air and condenses it into minute drops.

260. Chemical Properties. 1. *Stability.* Hydrogen chlorid is a stable compound. It neither burns nor supports combustion, although some oxidizing agents attack it forming water and liberating chlorin.

2. *As an Acid.* In water solution hydrogen chlorid forms *hydrochloric acid*. Concentrated hydrochloric acid contains about 38% of the gas by weight. If the solution is boiled hydrogen chlorid escapes until the solution contains only 20% of gas by weight; but when a more dilute solution is boiled water is given off and the solution becomes more concentrated until a 20% solution is formed. A 20% solution of hydrogen chlorid in water boils at 120° C. and its strength remains constant. Hydrochloric acid is one of the strongest acids known. It interacts with metals, oxids of metals, and bases to form *chlorids*.

261. Uses. Hydrochloric acid is used in the manufacture of chlorids, in making chlorin for the preparation of bleaching powder, and in cleaning metals. Many metals must be freed from oxids and other forms of corrosion before they can be plated or coated with other metals or enamels. The process of removing such scale or tarnish is known as "pickling." It consists in immersing the metals in an acid or a mixture of acids.

262. Chlorids. The chlorids form an important group of salts. Chlorids of nearly all the metals are known and

there are also many chlorids of non-metals, hydrogen, carbon, silicon, and sulfur for example, that are quite important compounds. The chlorids of the metals are generally crystalline salts. They are water soluble, except the chlorids of lead, silver, and mercurous mercury.

263. Test for Chlorids. If we add a few cubic centimeters of a solution of silver nitrate to a solution containing a chlorid, a white precipitate of silver chlorid is obtained. The precipitate is insoluble in nitric acid, but it dissolves in ammonium hydroxid. We may test for chlorids in this manner, but the test is not satisfactory when bromids or iodids are present.

264. Oxygen Acids of Chlorin. When we studied the method of naming acids, we learned that chlorin forms a whole series of acids containing oxygen. These acids are generally quite unstable and unimportant, but some of them form useful salts. The *chlorates* of sodium and potassium are used quite extensively, and the *hypochlorites* of sodium and calcium find extensive use.

265. Aqua Regia. If we mix nitric acid and hydrochloric acid, *aqua regia* is formed. Such metals as gold and platinum, which are not affected by ordinary acids, dissolve in this mixture. The chemical action is due to *nascent chlorin*. Nitric acid is a strong oxidizing agent, oxidizing the hydrochloric acid and liberating the chlorin. Since it is the chlorin thus set free in the nascent state that attacks the metals, *chlorids* are formed by dissolving metals in *aqua regia*. The most common proportion consists of 1 part of nitric acid to 3 parts of hydrochloric acid, although other proportions are often used.

C. BROMIN

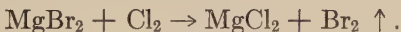
266. Occurrence. Several bromids are found in nature, the most abundant being the bromids of sodium and magnesium. The chief source of bromin is the "mother liquor"

from salt wells after the salt has been extracted. Bromids are also found in the extensive deposits of the salts of the alkali metals at Stassfurt, Germany. Bromin was used in nearly all the tear gases during the World War. The Allied Powers were handicapped when war gases began to be largely used because Germany and the United States have so nearly a monopoly of this element.

267. Preparation. The method of preparing bromin is analogous to that used in making chlorin. Any bromid may be treated with sulfuric acid and an oxidizing agent. Potassium bromid is usually used in the laboratory. Manganese dioxid serves as an oxidizing agent. The student should compare the following equation with that for the preparation of chlorin:



Commercially bromin is often prepared by decomposing bromids with chlorin:



The liquor containing the bromids flows down through a tower filled with balls of silica or other rock. As it trickles down over the rock it meets a current of chlorin gas and the reaction takes place as represented above. The principle of *counter currents* is quite widely used in chemical industry.

Bromin is extracted from the "mother liquor" of the salt wells of Ohio and Michigan by electrolysis.

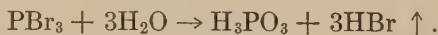
268. Physical Properties. Bromin is a dark red liquid about three times as heavy as water. It is quite volatile; its vapor has a very disagreeable odor (*bromus*, stench) and it irritates the eyes and throat. If the liquid comes into contact with the skin it produces frightful burns. Bromin is moderately soluble in water forming a reddish-brown solution which is used in the laboratory under the name of *bromin water*. Bromin water is an oxidizing agent.

269. Chemical Properties. Bromin resembles chlorin in its chemical properties, but it is less active. It unites directly with many metals forming bromids. With hydrogen it forms hydrogen bromid. Like chlorin, it is a bleaching agent when it is moist.

270. Uses of Bromin. In the manufacture of certain organic compounds, especially some of the dyestuffs, bromin is employed. The tear gases, which were used to temporarily blind the enemy during the war, nearly all contained bromin. *Xylyl bromid* is one of the compounds that was extensively used. The *bromids of sodium and potassium* are used in medicine as sedatives. *Silver bromid*, which is sensitive to light, finds use in photography.

271. Hydrogen Bromid. When we treat a bromid with sulfuric acid some hydrogen bromid is set free. But hydrogen bromid is more unstable than hydrogen chlorid and part of it decomposes from the heat of the reaction. Then the hydrogen thus formed reduces some of the sulfuric acid, so that the hydrogen bromid prepared in this way would be contaminated with bromin and sulfur dioxide.

Pure hydrogen bromid is prepared by the action of water on the tri-bromid of phosphorus:



Hydrogen bromid is a gas similar to hydrogen chlorid. It dissolves in water forming *hydrobromic acid*. The solution has all the properties of a strong acid.

D. IODIN

272. Source. At one time nearly all the iodine came from the seaweeds that were washed ashore. These weeds were burned and the iodine was then extracted from the ash that was left. This is still a source of iodine, but a greater amount is obtained from the nitrate beds in Chile.

273. Preparation. The manner of preparing iodine does not differ radically from that of preparing bromine and chlorine. Some iodine is treated with sulfuric acid and an oxidizing agent.



The iodine vaporizes and may be condensed as a solid on the walls of a cold dish or beaker.

274. Physical Properties. Iodine is a steel-gray, crystalline solid. When heated it *sublimes*, or vaporizes without first liquefying. Its vapor which is violet in color has an irritating odor, somewhat resembling that of chlorine. Iodine is very slightly soluble in water. It dissolves readily in alcohol, forming the *tincture of iodine*. In an aqueous solution of potassium iodide it is very soluble and it dissolves very readily in carbon disulfide, giving a beautiful violet or purple solution.

275. Chemical Properties. If we put a crystal of iodine on a piece of phosphorus the two elements combine spontaneously giving off heat and light. It also combines readily with other elements but it is less active than chlorine or bromine. When a solution of iodine is added to starch paste a blue color is produced. In this manner iodine may be used as a test for starch or the starch may serve as a test for iodine. The blue color disappears when the paste is heated, but it reappears when it is subsequently cooled. The iodine must be *free* to color starch paste.

276. Uses of Iodine. Iodine is used in medicine, in photography, and for making dyestuffs. *Iodoform* has the formula CHI_3 . The *tincture of iodine* contains 7% of iodine dissolved in alcohol or in a solution of potassium iodide. It is used as a counter-irritant to reduce swellings. If the *tincture* is too strong, or if the part painted with iodine is covered so the iodine can not evaporate, the skin may be blistered. Iodine is now used widely to sterilize wounds.

277. Hydrogen Iodid. If we try to prepare hydrogen iodid by the general method of preparing acids, we get little hydrogen iodid. When we heat an iodid with sulfuric acid, the unstable hydrogen iodid reduces a part of the sulfuric acid to hydrogen sulfid. Some free iodine is formed when the hydrogen iodid decomposes. The pure gas is prepared by the interaction of phosphorus, iodine, and water.

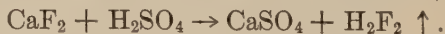


Hydrogen iodid is a colorless gas similar in its properties to hydrogen chlorid, but much less stable. It dissolves in water forming *hydriodic acid*. This solution has all the characteristics of a strong acid.

E. FLUORINE

278. Fluorine. Fluorine is the *most active* element known. It combines readily with practically all elements but oxygen. In its physical properties it resembles chlorine, but it is much more active chemically. Chlorine combines with hydrogen explosively in sunlight, but fluorine combines with hydrogen even in the dark. It attacks nearly all the metals, forming fluorides. It attacks gold and platinum very slowly. In the preparation of fluorine, reasoning by analogy leads us into error; *fluorine can not be prepared by oxidizing hydrogen fluoride* in a manner similar to the preparation of the other halogens. The only method known for preparing this element is the electrolysis of a fluoride, usually *potassium acid fluoride*, KHF_2 .

279. Hydrogen Fluoride is prepared by the action of sulfuric acid on calcium fluoride, a compound found in nature:



Like the other halogen compounds with hydrogen, it is a colorless gas that fumes strongly in moist air. It dissolves in water forming *hydrofluoric acid*. This acid is very corrosive, causing painful sores that heal very slowly. The

vapor is very dangerous if inhaled. Hydrofluoric acid attacks most ordinary substances, wax, lead, and platinum being the most common exceptions. At the ordinary temperature the molecular weight of the gas is 40, showing that its formula is H_2F_2 . At somewhat higher temperatures its molecular weight is only 20, corresponding to the formula HF .

The chief use of hydrofluoric acid is for etching glass. The glass is first covered with paraffin or wax; with a sharp

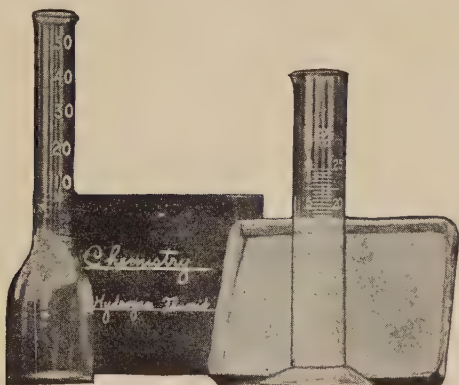


FIG. 126.—The word “chemistry” was etched with the gas hydrogen flourid; the other words with a solution of the gas.

stylus the paraffin is then removed from the part to be etched. This prepared glass is then exposed to the gas, hydrogen flourid, or covered with a solution of hydrofluoric acid until the etching is of the required depth. See Fig. 126. The excess acid is then washed off and the paraffin removed. If a solution is used the etching is smooth and transparent; if the gas is used it will be more or less rough and translucent.

Fluorids are used to some extent in “frosting” glass, in the making of enamels, and in the manufacture of certain kinds of glass.

280. Relative Stability of the Halogen Compounds. A study of the halogen compounds shows that the compounds

of fluorin are the most stable; chlorin compounds are next in stability, followed by those of bromin; iodin compounds are least stable. These facts seem obvious if we consider the relative activity of the different elements. The *heat of formation* also varies as the following heat equations show. The amount of heat liberated is for the formation of 1 mole of the hydrogen compounds:



In the preparation of hydrogen iodid at the ordinary temperature heat is absorbed, since the reaction is endothermic.

The fact that one halogen can replace another is also of interest as related to stability. If we add chlorin water to a solution of a bromid, the chlorin takes the place of the bromin as shown by the equation:



We have seen that this reaction is of importance in the commercial preparation of bromin. In a similar manner chlorin replaces iodine; and bromin replaces iodine:



These reactions are exactly what we might expect from the heat equations shown above. The last reaction may be strikingly shown since both bromine and iodine are much more soluble in carbon disulfid than they are in water.

If we add to a water solution of potassium iodid a few drops of carbon disulfid and shake thoroughly, neither the water layer nor the carbon disulfid will be colored since combined iodine does not color its solutions. Now if we

add a little bromin water and again shake the solution the carbon disulfid will be colored purple showing that the bromin has combined with the potassium and set free the iodine as represented in the equation above. Had the bromine remained free and dissolved in the disulfid a reddish-brown color would have been produced.

SUMMARY

Fluorine, chlorine, bromine, and iodine comprise the halogen group.

With the exception of fluorine, which is prepared by electrolysis, the halogens are all prepared by oxidizing the hydrogen acids of the respective elements.

The hydrogen acids of the halogens may be prepared by treating a salt of the acid required with sulfuric acid.

Chlorine is used for bleaching, disinfecting, as a disease preventive, and as a poison. *Bromine* is used in the dye industry and in the preparation of bromides. *Iodine* is used medicinally.

The following table shows comparatively the properties of the halogens:

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic weight.....	19	35.5	80	127
State.....	gas	gas	liquid	solid
Principal valence.....	1	1	1	1
Boiling point.....	— 187° C.	— 34° C.	59° C.	184° C.
Activity.....	most	less	still less	least
Formula of hydrogen acid	HF	HCl	HBr	HI
Stability of hydrogen acid	most	less	still less	least
Heat of formation of hydrogen acid.....	37,600	22,000	8,400	— 6,100
Replacement.....	replaces Cl, Br, and I	replaces Br and I	replaces iodine	

QUESTIONS

1. Compare the chemical action of chlorine, sulfur dioxide, ozone, and hydrogen peroxide as bleaching agents.

2. Balance and complete the following equations:



3. Can you see any advantage in having the bleaching powder and acid in separate vats in bleacheries?

4. Give two reasons why nitric acid is not suitable for use in making hydrogen chlorid.

5. Why do solutions of hydrogen iodid become dark-colored on standing?

6. Why should chlorin water be kept in dark-colored bottles?

7. From the source of bromin what do you judge to be the relative solubility of chlorids and bromids?

8. Hydrofluoric acid is put on the market in wax bottles. Explain.

9. How would you test for the presence of a fluorid, a chlorid, a bromid, and an iodid?

10. What is the meaning of the term "aqua regia"? Why is this name given to a mixture of nitric and hydrochloric acids?

11. If a metal is dissolved in aqua regia, what salt is usually formed?

12. How would you test for free iodin? For combined iodin?

13. Why do we not get metallic sodium when a solution of sodium chlorid is electrolyzed?

14. What precautions would you take if you were required to work with hydrofluoric acid?

15. Why is it impossible to remove, by the use of chlorin, spots made with printer's ink?

CHAPTER XXVI

PERIODIC LAW—ATOMIC NUMBERS

A. PERIODIC LAW

281. Classification of Elements. If the student were to study each element as an individual, his task would be quite difficult. To simplify chemistry, attempts to group elements have been made from time to time. We have already referred to elements as *metallic* and *non-metallic*, and we learned that some elements have to some extent the properties of both metals and non-metals. We have also mentioned the fact that some elements are *acid-formers*, and others are *base-formers*. The elements hydrogen, oxygen, carbon, nitrogen, sulfur, and the halogens are acid-formers. But here again *some* elements act as acid-formers under some circumstances, and as base-formers under different conditions. Such elements form *amphoteric* compounds which may act as either acids or bases.

Oxygen and sulfur are both acid-formers. If we study them more carefully, we find that they have other *chemical* properties in common. For example, both are very active at high temperatures. Both elements exist in allotropic modifications. Sulfids and oxids are much alike in their manner of formation, their solubility, their stability, and in the valence of the negative element.

A much more striking resemblance may be noted in the chemical behavior of the halogens. So similar are these elements that it is possible to predict with reasonable accuracy the chemical properties of one halogen from a knowledge of the characteristics of the family or group. Several other elements may be grouped into *families*.

282. Early Attempts at Classification. As early as 1817, Dobereiner grouped certain elements into *triads*. He observed that the differences between the atomic weights of chlorin, bromin, and iodine were practically constant. The same holds true for the atomic weights of calcium, strontium, and barium.

In 1864 Newlands grouped all the elements in the order of their increasing atomic weights, and then divided them into groups of seven elements each. He made the division into groups of seven, because the eighth element had properties similar to the first in the preceding group. Thus he discovered the *law of octaves*.

Lothar Meyer and Mendelejeff each worked out a complete system for grouping the elements according to their atomic weights. In their systems the first two periods have *seven* elements each. Then there are *long periods* of *seventeen* elements each.

283. Mendelejeff's Periodic Law. In this country the work of Mendelejeff, in his attempts to classify elements, is generally considered the most successful. He believed that the chemical properties of elements are functions of their atomic weights.

Omitting hydrogen, suppose we arrange the elements in the order of their atomic weights, and examine the first eight.

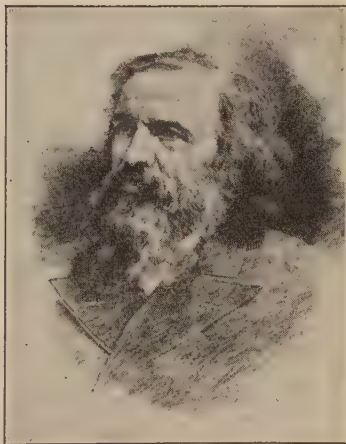
He	Li	Be	B	C	N	O	F
4	7	9	11	12	14	16	19

Helium is an inert element; lithium is metallic, a very strong base former; beryllium is metallic, a base former; boron may form a base, although it more often forms a weak acid; carbon forms a weak acid; nitrogen forms strong acids; oxygen is characteristically acid; and fluorine is the most active non-metal known. Thus these elements form a *series* where the base-forming properties decrease and the tendency to form strong acids increases.



Robert Wilhelm Bunsen (1811–1899) was a German chemist. For nearly forty years he was Professor of Chemistry at the University of Heidelberg. He was the inventor of many laboratory devices, including the Bunsen burner, a photometer, a voltaic cell, a filter pump, and a thermostat. His most important work was his discovery, with Kirchhoff, of spectrum analysis. By this method elements are detected, and new ones have been discovered. Bunsen discovered caesium and rubidium.

Dimitri Ivanovitch Mendeleeff (1834–1907) was a Russian chemist born in Siberia. He was Professor of Chemistry at the University of St. Petersburg. His "Elements of Chemistry" is a standard work and has been translated into English, German, and French. His most important work was the Periodic Law which deals with the classification of elements.



Now let us add to the above list the next eight elements, placing them in a new *series* below the first eight.

He	Li	Be	B	C	N	O	F
4	7	9	11	12	14	16	19
Ne	Na	Mg	Al	Si	P	S	Cl
20	23	24	27	28	31	32	35.5

Like helium, neon is inactive; sodium is also a strong base former resembling lithium; magnesium is similar to beryllium; aluminum is like boron; like carbon, silicon is a weak acid-forming element; phosphorus resembles nitrogen in its chemical properties; sulfur is like oxygen chemically; and chlorine is very active like fluorine.

By arranging all the elements in the order of their atomic weights Mendelejeff discovered that the properties of the elements recur at regular intervals. He therefore concluded that the properties of elements are periodic functions of their atomic weights. If we refer to the complete table, page 297, we find that the recurrence of properties causes certain families of elements, like the halogens, to fall in the same group. Thus in group 0 we find all the inactive elements. In group 1 we find the alkali metals, lithium, sodium, potassium, cesium, and rubidium. The nitrogen family, including nitrogen, phosphorus, arsenic, antimony, and bismuth, is found in group 5.

After the first two series, the period is longer before the recurrence of properties occurs, eighteen elements comprising the third series. The following series are also made up of long periods. At the bottom of each group in the following table, a general formula for the oxides of the elements comprising that group is given, as well as a general formula for the hydrides.

The student must not be confused by the fact that the periods now number eight and eighteen elements instead of seven and seventeen as in the original table. The inert

Period	Group 0	Group 1 A B	Group 2 A B	Group 3 A B	Group 4 A B	Group 5 A B	Group 6 A B	Group 7 A B	Group 8
1	He (4)	Li (7)	Be (9.1)	B (11)	C (12)	N (14)	O (16)	F (19)	
2	Ne (20)	Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)	
3	A (39.9)?	K (39.1) Cu (63.6)	Ca (40) Zn (65.4)	Sc (44.1) Ga (69.9)	Ti (48.1) Ge (72.5)	V (51.2) As (75)	Cr (52) Se (79.2)	Mn (54.9) Br (80)	Fe (56) Ni (58.7) Co (59)
4	Kr (83)	Rb (85.5) Ag (107.9)	Sr (87.6) Cd (112.4)	Yt (89) In (114.8)	Zr (90.6) Sn (119)	Cb (93.5) Sb (120.2)	Mo (96) Te (127.5)	 I (127)	Ru (101.7) Rh (102.9) Pd (106.7)
5	Xe (130.2)	Cs (132.8) Au (197.2)	Ba (137.4) Hg (200)	La (139) Tl (204)	Ce (140.2) Pb (207.1)	Ta (181) Bi (208)	W (184)		Os (190.9) Ir (193.1) Pt (195)
6	Nt (222)		Ra (226)		Th (232.4)		U (238.5)		
Oxids..... Hydrides.....		R ₂ O RH	RO RH ₄	R ₂ O ₃ RH ₃	RO ₂ RH ₄	R ₂ O ₅ RH ₃	RO ₃ RH ₂	R ₂ O ₇ RH	RO ₄

elements of Group 0 were unknown when Mendelejeff proposed his table.

284. Two Families in a Group. In the foregoing table it will be seen that in the long periods there are two families in a group, A and B. The elements of family A, lithium, sodium, potassium, rubidium, and caesium, have properties similar to each other, but they are less like copper, silver, or gold, elements of family B in the same group. Likewise in Group 2 the elements calcium, strontium, and barium are very similar to one another, but less like the elements of family B in the same group, zinc, cadmium, and mercury.

In the periodic table, page 299, the two families are clearly shown. Lithium and sodium belong to family A, but they are placed on a slanting line to indicate their relation to the elements of family B. In Group II beryllium has properties similar to those of the elements of both families. While magnesium resembles the elements of family B, it is more like calcium in its chemical behavior. The atomic number of each element is given in this table.

285. Value of the Periodic Law. 1. *It Simplifies Chemistry.* We have already seen that the grouping of elements into families makes the study of the properties and behavior of elements less difficult to grasp and retain.

2. *It Serves as a Check on Atomic-weight Determinations.* When the periodic table was first prepared several of the elements were not properly placed. The suggestion that this might be due to errors in the atomic-weight determinations seemed plausible. More accurate methods were used, giving new values for certain atomic weights. Upon the substitution of these new values many elements then fitted into their proper places in the table.

3. *In the Prediction of New Elements.* There are several gaps in the table, which led Mendelejeff to predict the existence of undiscovered elements, having properties and atomic weights that make them fit into these gaps. In

fact, within a few years immediately following the announcement of Mendeleeff's law several elements were discovered whose properties and atomic weights are very nearly in accord with what he had predicted. The remarkable agreement between the predicted properties of *eka-aluminum* and the actual properties of *gallium* are shown in the following table:

	Predicted	Discovered
Atomic weight.....	About 69	69.9
Melting point.....	Low	30.2°
Specific weight.....	5.9	5.95
Formula of oxid.....	X ₂ O ₃	Ga ₂ O ₃
Action of air.....	None	Slight, even at red heat

Since this element was discovered in France, it was named gallium. Mendeleeff also predicted the properties of *eka-boron* (scandium) and *eka-silicon* (germanium) with practically equal accuracy. Other elements, more recently discovered, have found places in the table.

B. ATOMIC NUMBERS

286. Atomic Numbers. The idea of atomic numbers was conceived in 1913 by Moseley, a brilliant young English chemist who lost his life in the World War. His system is based upon the spectra produced by X-rays coming from different metals. These reflected rays give spectra with well-marked lines which are characteristic of the metal from which they come. By photographing the spectra, it is possible to determine the frequency or the vibration rate of the rays that are characteristic of any given metal. From such frequency a factor known as the "Q" value may be calculated for each metallic element. See Fig. 127.

When the atomic number 1 is assigned to hydrogen, then

the atomic numbers of the other elements are in the sequence of their "Q" values. For example,

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
H	He	Li	Be	B	C	N	O	F
(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	
Ne	Na	Mg	Al	Si	P	S	Cl	

The atomic numbers of the gaseous and liquid elements can not be determined directly by the method just given.

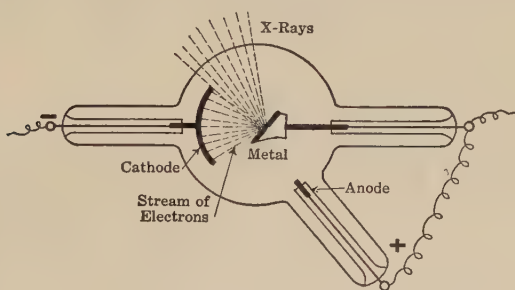


FIG. 127.—X-ray tube.

They may be found indirectly from the compounds of these elements with the metals.

287. Protons and Electrons. The theory that atoms are quite complex structures is now generally accepted. The modern conception of the atom assumes that it is made up of *protons* (unit positive charges of electricity) and *electrons* (unit negative charges). Let us refer to the chlorin atom for illustration. The largest part of the mass of the chlorin atom is believed to be made up of a *nucleus* containing 17 more protons than electrons. The excess of protons over electrons in the nucleus of any atom is the same as its atomic number.

There are also 17 *planetary* or *external* electrons grouped around the nucleus of the chlorin atom. If we accept Dr.

Bohr's theory of the structure of atoms, these electrons revolve about the nucleus in a manner somewhat analogous to that of the planets as they revolve about the sun. The number of external electrons is the same as the number of excess protons in the nucleus; therefore the atom is electrically neutral. *Thus the atomic number of an element is the same as the number of external electrons grouped around its nucleus.*

288. Isotopes. In Chapter XI we studied Dalton's atomic theory, which assumes that the atomic weight of an element is always the same. Recent experiments show that Dalton's theory is not entirely correct. By physical methods, several investigators have succeeded in separating chlorin of atomic weight 37, from chlorin which has an atomic weight of 35. The two *isotopes*, as they are called, have the same chemical behavior in every respect. They have the same atomic numbers but they differ in atomic weights. *Thus the chemical properties of an element seem to depend upon its atomic number rather than upon its atomic weight.* Ordinary chlorin, which has an atomic weight of 35.46, is probably a mixture of two or more isotopes.

Several elements, especially those whose atomic weights are not whole numbers, appear to be made up of two or more isotopes. The atomic weight of an element as we use it in the laboratory is probably an average of the atomic weights of its isotopes.

289. Atomic Numbers and the Periodic Law. In the periodic table as shown on page 297, we find that it is necessary to place argon (39.9) before potassium (39.1) in order to have a recurrence of the chemical properties of certain groups. Potassium certainly belongs in the sodium family and argon in the group of inert elements. In a similar manner we must place tellurium (127.5) before iodine (127) in the table, since the former resembles sulfur in its chemical behavior, and iodine undoubtedly belongs in the halogen

family. Thus we see that Mendelejeff's law is not entirely correct when we consider the chemical properties of an element as related to its atomic weight.

The table shown on page 299 has the elements arranged in the order of their atomic numbers. The atomic number of argon is 18 and of potassium 19. Hence the elements appear in the proper place in the table when arranged in the order of their atomic numbers. In the light of atomic numbers, we therefore modify the periodic law as follows: *The chemical properties of elements recur after certain intervals when the elements are arranged in the order of their atomic numbers.*

SUMMARY

Elements are grouped as *metals* and *non-metals*; they are also classed as *acid-forming* elements and *base-forming* elements.

Mendelejeff arranged the elements in the order of their atomic weights. He then formulated the law that the *properties of elements are periodic functions of their atomic weights.*

The periodic law is of value: (1) in classifying elements and thus simplifying the study of chemistry; (2) it serves as a check upon the accuracy of atomic-weight determinations; (3) it indicates the presence of undiscovered elements in the earth's crust and has on several occasions enabled accurate predictions to be made concerning the properties and atomic weights of elements then undiscovered.

By the use of X-ray spectra Moseley worked out a system of *atomic numbers* for the elements. The chemical behavior of an element seems to bear some relation to its atomic number.

Atoms are believed to consist of a nucleus containing an excess of protons surrounded by external electrons. *The number of external electrons is the same as the atomic number.* The table of elements based upon atomic numbers explains chemical facts better than the table based upon atomic weights.

QUESTIONS

1. If an element were discovered having an atomic weight less than copper and greater than cobalt, what properties would you expect it to have?

2. Write the formula for the oxid, hydroxid, sulfate, and carbonate of strontium.

3. Aluminum hydroxid is insoluble in water. What would you infer as to the solubility of the hydroxid of scandium?

4. What properties would you expect cæsium to have?

5. How can you use the periodic table in your study of chemistry?

6. From the table pick out several elements that you would expect to form strong bases. Several that will form strong acids.

7. Name several elements that you would expect to be isotopes.

8. From the modern theory of atomic structure how does an atom become a positive ion? A negative ion?

9. Why is a periodic table based upon atomic numbers more valuable than a similar table based upon atomic weights?

CHAPTER XXVII

THE NITROGEN FAMILY

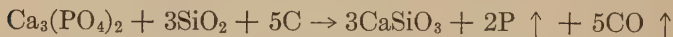
290. Nitrogen Family. The most important element of this family, *nitrogen*, has already been studied. The other four elements in this family, *phosphorus*, *arsenic*, *antimony*, and *bismuth*, are quite similar in their chemical behavior to nitrogen. The acid-forming properties of the group decrease from nitrogen to bismuth. Nitrogen forms one of the strongest acids known. Phosphoric acid is weaker, while antimony and bismuth may act as base-formers in the presence of strong acids. The valence of the elements in this family is usually 3 or 5.

A. PHOSPHORUS

291. Occurrence. The element phosphorus never occurs free in nature. The most important compound is rock phosphate, or *calcium phosphate*. The bones and teeth of animals contain calcium phosphate. This phosphate is present to some extent in all fertile soils, and extensive areas of rock phosphate are found in Florida, Tennessee, and South Carolina. Enormous deposits have been discovered in the Northern Rockies near Yellowstone Park, but the phosphate industry is still undeveloped in this area.

292. Preparation. Phosphorus is extracted from calcium phosphate by heating this compound with sand and coke in an electric furnace. A mixture of these substances is fed into the furnace by a worm conveyor *C* as shown in Fig. 128. The resistance of the mixture between the electrodes *E* and *E'* is great enough so that much of the electrical energy is

converted into heat energy. At the high temperature which is produced the following chemical reaction occurs:



The calcium silicate forms a slag which is drawn off at *S*. The phosphorus and carbon monoxid pass out of the furnace

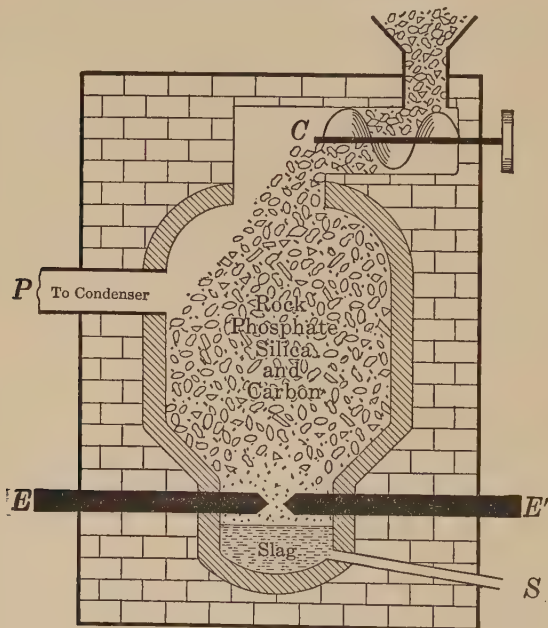


FIG. 128.—Electric furnace for making phosphorus.

through the opening *P*. The phosphorus vapor is condensed by water and cast into sticks.

293. Properties. Phosphorus exists in two important allotropic forms: *white* or *yellow* phosphorus, and *red* phosphorus.

A. White Phosphorus. When freshly prepared, phosphorus is nearly colorless or a pale straw color. Since it is

usually a pale lemon color it is often known as yellow phosphorus. White phosphorus is a waxy, translucent solid, nearly twice as dense as water. It melts at $44^{\circ}\text{C}.$, but since its kindling temperature is only $35^{\circ}\text{C}.$, it must be melted under water to prevent combustion.

White phosphorus must never be handled with the fingers, since burning phosphorus produces poisoned wounds that require a long time to heal. It is very poisonous if taken internally, a small fraction of a gram being a fatal dose. White phosphorus is soft enough to be easily cut with a knife, but *it must always be cut under water* to prevent the heat from the friction of the knife from enkindling it. Phosphorus is insoluble in water, but the white phosphorus dissolves readily in carbon disulfid and in oils.

Phosphorus oxidizes readily when exposed to the air, giving off dense white fumes of phosphorus pentoxid, P_2O_5 . If this oxidation occurs in a dark room a faint glow or *phosphorescence* can be seen. To prevent oxidation phosphorus is always kept under water. In oxygen phosphorus burns with dazzling brilliancy. Heated to a temperature of $250^{\circ}\text{C}.$ without access to air, or upon exposure to sunlight, it changes to red phosphorus.

B. Red Phosphorus. This form of phosphorus is a dark red powder. It is slightly more than twice as dense as water. It is insoluble in water or in carbon disulfid.

Red phosphorus is not poisonous; it does not take fire when exposed to the air; its kindling temperature is about $250^{\circ}\text{C}.$, phosphorus pentoxid being formed as it burns. When heated without access to air to a temperature of about $290^{\circ}\text{C}.$, it sublims and forms yellow phosphorus upon condensation.

294. Uses. Some phosphorus is used as a poison for rats, mice, and other vermin. Great care must be taken to see that food is not contaminated by such poisons. Small quantities of phosphorus find use in making special alloys

with copper and tin. Phosphor bronze is not corroded by water.

Because it takes fire at so low a temperature, phosphorus was used in the World War in explosive shells and hand grenades that were designed for incendiary purposes. Incendiary bullets were very effective in bringing down Zeppelins which contained hydrogen in their gas bags. Tracer bullets also used phosphorus.

In burning, phosphorus produces dense white clouds of phosphorus pentoxid. Therefore it was one of the most effective smoke screens used during the War.

Two large industries use the bulk of the phosphorus that is produced; the match industry and the fertilizer industry.

295. Matches. The old friction match was tipped with white phosphorus. In the manufacture of such matches many workmen suffered from a disease which produced a decay of the bones. This disease, which usually attacked the jaw-bones through decayed teeth, was caused by the inhalation of the vapors of phosphorus. Children were frequently poisoned by sucking the heads from such matches. In 1913 a law was passed imposing a prohibitive tax (2 cents per 100 matches) upon the old white phosphorus match. Their use is now forbidden in most civilized countries.

Two types of matches are now in common use: (1) the friction match which "strikes anywhere"; and (2) the safety match. In the manufacture of the ordinary friction match the stick is dipped in molten paraffin so that it will burn more easily. Then it is dipped into a paste consisting of glue, a filler, and some oxidizing agent such as potassium chlorate or lead dioxid. For the tip of the match *phosphorus sesquisulfid*, P_4S_3 , serves just as well as the white phosphorus and it is non-poisonous.

The head of the ordinary *safety* match consists of antimony trisulfid, Sb_2S_3 , some oxidizing agent such as potassium chlorate, and glue. The box is covered with a layer of red

phosphorus, powdered glass, and glue. Such matches do not readily ignite except by rubbing them on this preparation on the box. The wood is usually impregnated with a fireproofing material to prevent after-glow.

296. Oxids of Phosphorus. Two oxids of phosphorus are known: *phosphorous oxid*, P_2O_3 , is formed when phosphorus burns in a limited supply of air; *phosphoric oxid*, P_2O_5 , a white solid, is formed when phosphorus burns in air or oxygen. This oxid has a great affinity for water and does not combine readily with many gases, hence it is used extensively for drying gases.

297. Acids of Phosphorus and Their Salts. Of several acids of phosphorus, *ortho-phosphoric acid*, H_3PO_4 , is the most important. It may be formed by dissolving phosphoric oxid, its anhydrid, in water, but it is usually prepared commercially by the action of sulfuric acid on a phosphate.



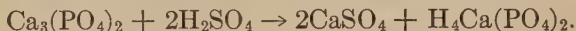
Phosphorous acid has the formula H_3PO_3 ; its anhydrid is phosphorous oxid, P_2O_3 . *Pyrophosphoric acid*, $H_4P_2O_7$, *metaphosphoric acid*, HPO_3 , and *hypophosphorous acid*, H_3PO_2 , are all known.

The acids of phosphorus are not used very extensively, but some of their salts are very important. Phosphoric acid, being a *tri-basic acid*, forms three classes of salts. To illustrate, *tri-sodium phosphate*, Na_3PO_4 , *di-sodium phosphate*, Na_2HPO_4 , and *mono-sodium phosphate*, NaH_2PO_4 , are well-known salts of phosphoric acid. Certain phosphates and several of the hypophosphites are used in medicines.

298. Phosphates as Fertilizers. Plants and animals both need phosphorus, plants taking phosphorus from the soil, while animals are dependent upon plants for their supply. Most soils contain a greater or less supply of phosphorus in the form of phosphates. By continual cropping, the soil

may be deprived of its phosphorus just as we have seen that a soil may have its nitrogen compounds removed. For this reason practically all *artificial fertilizers* contain phosphates.

These phosphates may be obtained from *guano*, *fish scrap*, *ground bone*, or as is more often the case, from *rock phosphates*. The phosphate rock is treated with sulfuric acid to convert insoluble *tri-calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$, into an acid calcium phosphate, usually $\text{H}_4\text{Ca}(\text{PO}_4)_2$, which is soluble and can be absorbed by plants. The reaction is as follows:



This *mono-calcium phosphate* is often called *super-phosphate of lime*. The *calcium sulfate* formed is rather beneficial to plants.

Generally not enough sulfuric acid is used to convert all the tri-calcium phosphate into the super-phosphate and these two compounds then slowly interact to form *reverted calcium phosphate*, $\text{H}_2\text{Ca}_2(\text{PO}_4)_2$, a compound insoluble in water, but soluble in water containing carbon dioxide or in certain soil acids. This compound is not available for immediate use but it is slowly converted into a plant food.



The analysis of an artificial fertilizer should show not only the amount of phosphorus present equivalent to *total phosphoric acid*, but it should show what per cent is equivalent to *insoluble phosphoric acid*, the per cent equivalent to *soluble phosphoric acid*, and the per cent equivalent to *reverted phosphoric acid*.

B. ARSENIC

299. Occurrence. Some arsenic is found uncombined in nature. More often it is found as the sulfid or associated with the ores of other metals, especially copper and iron.

300. Preparation and Properties. Most of the arsenic is obtained as a by-product from smelters. In roasting certain sulfid ores the arsenic they contain is oxidized and condenses in the flues of the smelter. It is removed and reduced with carbon to metallic arsenic.

Arsenic is a gray solid with a metallic luster. In its physical properties it resembles the metals, but chemically it behaves like the non-metal phosphorus, although it is less active. Heated in the air it burns with a blue flame forming *arsenious oxid*, As_2O_3 , commonly called *white arsenic*. Arsenic unites with nascent hydrogen to form arsine, AsH_3 , a very poisonous gas with a garlic-like odor. Use is made of this reaction in Marsh's test for arsenic, an exceedingly delicate and reliable test for this element. The test is important since nearly all compounds of arsenic are very poisonous.

301. Uses of Arsenic and Its Compounds. The metal arsenic is used in hardening shot and in the manufacture of some kinds of glass. White arsenic is used as an insecticide, especially by taxidermists. Certain compounds of arsenic are used medicinally. Scheele's green is a pigment that contains arsenic. Arsenic pigments are usually slightly volatile and such vapors are poisonous. Paris green, a compound containing arsenic and copper, is used as an insecticide.

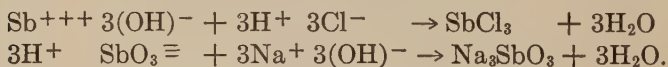
Arsenic forms acids exactly analogous to those formed by phosphorus. For example, H_3AsO_3 is *arsenious acid*; H_3AsO_4 is *arsenic acid*. Some arsenites and arsenates are important compounds. Enormous quantities of *arsenate of lead*, $\text{Pb}_3(\text{AsO}_4)_2$, are used every year for spraying trees to destroy such noxious insects as the gypsy and brown-tail moths. Air-planes have been used to spray the cotton-fields with *calcium arsenate*, $\text{Ca}_3(\text{AsO}_4)_2$, in an effort to check the ravages of the cotton-boll weevil. Arsenic compounds were used during the World War as poison gases, and more extensively in making the "sneeze" gases which were designed to force the removal of the gas-masks.

C. ANTIMONY

302. Occurrence. Antimony occurs free in nature to some extent. Commercially antimony is obtained from *stibnite*, Sb_2S_3 , a sulfid of antimony which is quite widely distributed. In the United States antimony is obtained from "antimonial lead ores."

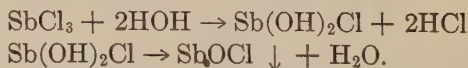
303. Properties. Antimony is a silver white element with a bright metallic luster; it is quite heavy and very brittle. It is less active chemically than arsenic, but when heated in the air it forms the trioxid, Sb_2O_3 , a white volatile solid. With nascent hydrogen it forms *stibine*, SbH_3 , a compound analogous to *arsine*. Antimony is not affected by hydrochloric acid, but it dissolves slowly in aqua regia forming a chlorid. Like arsenic, it forms a series of weak acids.

The hydroxid of this element is *amphoteric*, since under some circumstances it forms an acid and under other circumstances it forms a base. To illustrate, its hydroxid may ionize as in the following equations:



Thus we see that the hydroxid of antimony acts as a base in the presence of a strong acid like hydrochloric. In the presence of a strong base like sodium hydroxid the hydroxid of antimony acts as an acid and forms antimonites. *The hydroxids of several elements are amphoteric and behave in a similar manner.*

If we put antimony tri-chlorid in water, it not only hydrolyzes but dehydration occurs and a new type of compound is formed as represented by the equations:



At first a basic chlorid is formed, but it decomposes forming the *oxy-chlorid*, SbOCl , sometimes called the sub-chlorid.

304. Alloys. By melting together two or more metals a substance, called an *alloy*, is often formed. In some cases an alloy appears to be merely a mixture of metals; in other cases a compound appears to be formed, since the proportion is definite. Many of the alloys are solid solutions of metals in one another. When such alloys are cooled, crystals of one of the metals may separate. Fig. 129 shows a photo-micrograph of an alloy of antimonial lead. Crystals of antimony may be seen embedded in the metallic lead.



FIG. 129.—Antimonial lead. Magnified 75 diameters.

An alloy may have properties quite unlike those of any of its constituents, or in some cases they may be intermediate. Usually the melting point of an alloy is lower than the average melting point of its constituents and often it is below that of any one of them.

305. Uses of Antimony. Antimony is used in preparing several alloys. *Type-metal* contains antimony, lead, and tin; the antimony is especially important since it expands when it solidifies, and the type is thus made distinct and clear-cut. Antimony is also used in the non-friction alloys such as *Babbitt's metal* or *antimonial lead*. *Britannia metal*, an alloy much used in making tableware, is an alloy of antimony, tin, copper, and often zinc. Finely divided antimony under the name of *antimony black* is used for coating plaster casts to give them a metallic appearance.

The *sulfids of antimony* are used as pigments. They also find use in vulcanizing rubber; red rubber contains antimony.

Tartar emetic is a compound of antimony that is used as a mordant in the dyeing of cotton goods.

D. BISMUTH

306. Bismuth. Bismuth is a heavy metal that resembles antimony to considerable extent. It has a distinctly reddish hue. It is more metallic than antimony and forms bases more readily.

The chief use of bismuth is in the manufacture of the *fusible* alloys. Two common ones, Wood's metal and Rose's metal, melt at temperatures below that of boiling water.

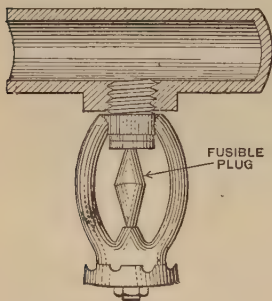


FIG. 130.—Automatic sprinkler.

The fusible alloys are used as safety plugs in boilers, as fuses in electric wiring, in fire alarms and automatic sprinkling devices, and for automatically closing the doors of fireproof safes. See Fig. 130.

Bismuth acts as a trivalent element in the formation of most of its compounds. It acts in the same manner as antimony when its salts are treated with water, hydrolysis first occurring and then dehydration. Thus the chlorid, BiCl_3 , forms an *oxy-chlorid* or *sub-chlorid*, BiOCl , when treated with water. The *sub-nitrate*, BiONO_3 , is used in medicine.

SUMMARY

Of the allotropic forms of phosphorus, the white variety and the red are the most common. *White* phosphorus is very active, even at the ordinary temperature. *Red* phosphorus is quite inert.

Phosphorus is used as a *poison*, in making *matches*, and as a constituent of certain *alloys*.

The phosphates of calcium are important constituents of commercial fertilizers.

Arsenic is used for hardening shot; its compounds are used to some extent in medicines, for pigments, and as insecticides.

Antimony forms several alloys, the following being the most important: *type-metal*, *Babbitt metal*, and *Britannia metal*.

Bismuth is used in the manufacture of *fusible alloys*; its salts are used for medicine.

The following tabular form shows the rather close relationship between the elements of the nitrogen family.

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weights.....	14	31	75	120	208
Valence.....	3, 5 In oxids some	3, 5 of the ele	3, 5 ments have	3, 5 a valence of	3, 5 1, 2, or 4
Hydrids.....	NH ₃	PH ₃	AsH ₃	SbH ₃	
Oxids.....	N ₂ O ₃ N ₂ O ₅	P ₂ O ₃ P ₂ O ₅	As ₂ O ₃ As ₂ O ₅	Sb ₂ O ₃ Sb ₂ O ₅	Bi ₂ O ₃ Bi ₂ O ₅
Acids.....	HNO ₂ HNO ₃	H ₃ PO ₃ H ₃ PO ₄	H ₃ AsO ₃ H ₃ AsO ₄	H ₃ SbO ₃ H ₃ SbO ₄	
	Very strong acids	Weak acids	Weak acids	Very weak acids	Basic

QUESTIONS

1. Why have laws been passed in many countries forbidding the use of white phosphorus for making matches?

2. If a solution of phosphorus in carbon disulfid is poured on a piece of filter paper, spontaneous combustion takes place as soon as the disulfid evaporates. Explain.

3. How does the strength of the acids in this family seem to relate to the atomic weights? How does it appear to vary with the valence?

4. How could you prepare red phosphorus from the white? How could you prepare white phosphorus from the red?

5. Why should the analysis of a fertilizer show the per cent of each phosphate present as well as the total amount?

6. Under what circumstances does the hydroxid of antimony act as a base? When does it act like an acid?

7. How do you account for the fact that antimony and bismuth occur free in nature while phosphorus never does?

8. Why is the use of arsenic as a pigment in wall papers forbidden?

9. Write the formulas for three calcium phosphates. Write the formula for sodium arsenite; for sodium arsenate.

10. How should white phosphorus be stored? What precautions should be taken in handling white phosphorus?

11. Explain how fusible alloys are used with fire-doors. How does a fusible plug protect a steam boiler in an ordinary furnace?

12. How does a friction match differ from a safety match?

13. Explain the action of the automatic water sprinkler in extinguishing fires.

14. Why is phosphorus essential to animal life? Where do we get our phosphorus?

CHAPTER XXVIII

CHEMISTRY IN THE WORLD WAR

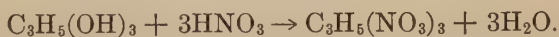
307. Introductory. More and more modern warfare has become dependent upon chemistry. Several times we have referred incidentally to the applications to war uses of some of the compounds that we have studied. Many persons are disposed to believe that the entire science of chemistry had to be revised in the light of war research. Such is not the case, since the same principles hold in the manufacture of war chemicals that are used daily in times of peace. Some new compounds were manufactured and many compounds that had been known for years but little used were made on an enormous scale for military purposes. Several compounds were put to entirely new uses. In this chapter we shall study certain compounds that are commonly known as war chemicals and then show how many of them can be used for other purposes since the close of the World War.

A. EXPLOSIVES

308. Black Gunpowder. Centuries before gunpowder was used in Europe it is said to have been known in China. As early as the first part of the fourteenth century it appeared in Europe. Gunpowder is made by mixing 75 parts of potassium nitrate with 15 parts of charcoal and 10 parts of sulfur. The powdered mixture is moistened and pressed into a cake by means of a hydraulic press. It is then broken up into grains of the desired size. Gunpowder is used as a *priming* charge in firing the so-called "smokeless powder."

309. Nitroglycerin. This explosive was discovered by Sobrero in 1846, but it was not developed until 16 years later

when Nobel devised a practical method of making it. It is said that Nobel founded the "Peace Prize" when he realized the possibilities for evil in certain explosives he had invented. *Nitroglycerin*, or *glyceryl nitrate*, is made by treating glycerin with a mixture of nitric and sulfuric acids. The sulfuric acid absorbs the water as it is formed.



Nitroglycerin is a heavy oily liquid. In the open air it burns readily. Since one molecule has more than enough oxygen to combine with all its carbon and hydrogen, it burns without access to air forming water vapor, carbon dioxide, nitrogen, and oxygen. Such compounds are said to explode by *detonation*. Since the gases that are formed occupy many times the volume of the explosive, tremendous pressure is exerted by the decomposition of such explosives.

310. Dynamite. This explosive was invented in 1866 by Alfred Nobel. Infusorial earth consists of the microscopic skeletons of certain one-celled animals. This siliceous matter will absorb from 40 to 75% of nitroglycerin, thus forming *dynamite*. Wood pulp is also used as an absorbent. Sticks of dynamite are much safer to handle than the liquid nitroglycerin.

311. Nitrocellulose. In 1846 guncotton, or nitrocellulose was discovered by Schönbein. Cotton fibers consist of nearly pure cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$)_x. When nitric acid acts on cotton a series of nitrates is formed. A mixture of *concentrated* nitric and sulfuric acids acts on cotton forming *cellulose hexa-nitrate*, $\text{C}_{12}\text{H}_{14}\text{O}_4(\text{NO}_3)_6$. More *dilute* acid gives lower nitrates of cellulose. For use in making smokeless powder, the acid is made just strong enough to give a nitrate of cellulose that contains a little less than 13% nitrogen. With ether such a nitrate forms a plastic mass which may be pressed into various shapes and cut into different-sized grains of powder. See Fig. 131. The smokeless powder

produces carbon dioxid, carbon monoxid, water vapor, and nitrogen when it burns. Since these are all gaseous, no smoke is produced. This powder is also superior to the black gunpowder because it is more powerful, thus making a gun more efficient with a smaller weight of ammunition.

The lower nitrates of cellulose dissolve readily in a mixture of alcohol and ether forming *collodion*. It is used in surgery as liquid court plaster, or "New Skin." Collodion also finds use in photography. *Celluloid* is made by treating the lower nitrates of cellulose with camphor. *Pyralin* is a plastic of similar composition. The cellulose nitrates are often incorrectly called nitrocelluloses. *Blasting gelatin* is an exceedingly powerful explosive made by dissolving nitrocellulose in nitroglycerin.

312. Picric Acid is a yellow crystalline solid that is made by the action of nitric acid on *phenol*, or *carbolic acid*, C_6H_5OH . It is a tri-nitro-phenol having the formula $C_6H_2OH(NO_2)_3$. Picric acid and its salts are very explosive. It was a favorite explosive with the French, being used under the names *lyddite* and *mellinite*.

313. Tri-nitro-toluol (T. N. T.) is a comparatively new explosive that was introduced just a short time before the beginning of the late war. It is made by treating toluol, C_7H_8 , a coal-tar product, with a mixture of nitric and sulfuric acids. It has the formula $C_7H_5(NO_2)_3$. T. N. T. is a colorless

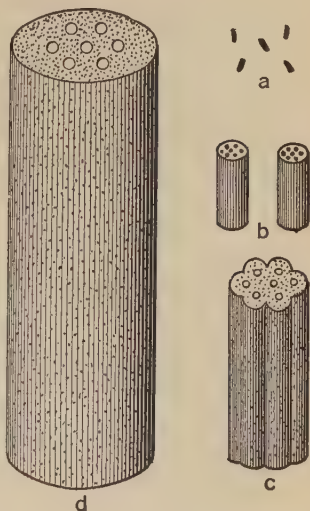


FIG. 131.—Grains of smokeless powder. *a*. Rifle powder. *b*. For 3-in. gun. *c*. For 6-in. gun. *d*. For 12-in. gun. (Actual size).

solid which darkens upon exposure to air. It can not be used as a powder, but it is a very satisfactory explosive for use in hand grenades, high explosive shells, depth bombs, torpedoes, and mines. It can be melted with safety and poured into the shells.

314. Ammonium Nitrate was used to considerable extent as an explosive during the war. It was generally mixed with some other explosive, T. N. T. for example. The name *amatol* was given to an explosive which contains a mixture of these two compounds.

315. Mercury Fulminate, or fulminating mercury, is always used as a *detonator*. For exploding any kind of powder or high explosive a small cap or cartridge is filled with mercury fulminate. The fulminate explodes with a sudden shock and thus causes the powder to explode by detonation. This compound, $\text{HgC}_2\text{N}_2\text{O}_2$, is made by treating mercury with nitric acid in the presence of alcohol. It is one of the most treacherous of explosives, since it may be exploded by heat, shock, or friction. While the chemistry of explosives seems very simple, the technique is complicated, and *no amateur should ever try to make any explosive*.

B. POISON GASES

316. Introductory. The name poison gas is given to certain war chemicals, many of them liquid or solid, whether they are really toxic or not. For example, such chemicals were used for various purposes. Some of them were lethal; some lachrymatory, affecting the eyes; others caused sneezing or vomiting; and still others irritated the skin causing blisters.

At first the gases were released from cylinders to be carried by the winds into the enemy trenches. Later they were incorporated in bursting shells. In either case a gas to be effective must be *heavy, active even when mixed with large proportions of air, not easily nullified by gas-masks, and quite persistent*.

317. Chlorin. The first poison gas to be used in the World War was chlorin. See section 257. As a cloud gas it was effective since it is about $2\frac{1}{2}$ times as dense as air. See Fig. 132. But it is quite a simple task to make a mask that will furnish adequate protection against chlorin, hence more



FIG. 132.—Photograph showing actual trench warfare.

deadly and dangerous gases came into use a little later. Nearly all of them are compounds of chlorin.

318. Phosgene. COCl_2 . This very toxic gas was used very extensively. It is made by combining carbon monoxid and chlorin in the presence of charcoal as a catalyst. Phosgene may be easily liquefied. It is an especially treacherous gas, since a man who inhales it does not suffer from it for several hours. Then he may collapse suddenly. It is suffocating and attacks the membranes of the respiratory organs and also tends to stop the action of the heart.

319. Chlor-picrin. CCl_3NO_2 . This compound is made by the interaction of bleaching powder and picric acid. It

is a heavy liquid that gives off a suffocating vapor, which attacks the eyes and also induces vomiting. Thus the men who inhaled its vapor were forced to remove their masks. Other more deadly gases were generally used with chlor-pierin.

320. Mustard Gas. $(C_2H_4Cl)_2S$. The so-called "mustard gas," known to chemists as *di-chlor-ethyl-sulfid*, is really an oily liquid. It caused more suffering and a larger number of casualties than all the other gases combined. This liquid is made by absorbing ethylene, C_2H_4 , in sulfur monochlorid, S_2Cl_2 . Mustard gas blisters the skin and causes wounds that heal slowly. As it slowly evaporates, a vapor is emitted which affects the lungs in a manner similar to pneumonia.

321. Special Gases. We have already seen that chlor-pierin is a *tear gas* which also causes vomiting. Several other

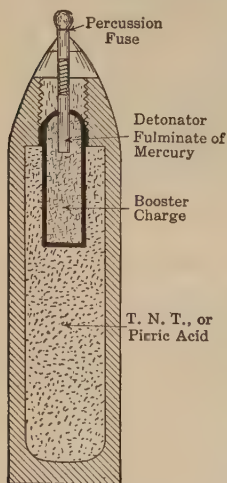


FIG. 133.—Shell filled with explosive.

tear gases were used to cause temporary blindness. Nearly all such gases contain bromin. *Xylyl bromid* is a tear gas that causes such a copious flow of tears that the victim is temporarily blinded even when the gas is present to the extent of only two or three parts per million of air. *Brom-acetone* is also a tear gas. The French also used *brom-benzyl-cyanid*. A very deadly gas included in this group is *tri-chlor-methyl-chloroformate*, commonly known as *diphosgene*.

To force the removal of gas masks, *sneezing gases* were introduced. They are usually compounds of arsenic. The most important one is *di-phenyl-chlor-arsine*. This compound is a solid that was embedded in the T. N. T. of a high explosive shell. See Fig. 133. When the explosion occurred very

small particles of this compound were scattered in all directions. These particles penetrated the mask and caused violent sneezing.

322. Flame Throwers. Another war development which was used to harass the enemy makes use of tanks from which burning oil is forced to a distance of 20 or 30 yards by compressed nitrogen. They were quite effective in weakening the morale of the men.

C. DEFENSIVE MEASURES

323. Introductory. As soon as a new offensive weapon or chemical appeared, chemists immediately began to search for a method of defense. In section 257 we learned how quickly temporary masks were made to nullify the effects of chlorin. Camouflage became an art in itself. "Smoke screens" were extensively used and improvements in gas masks were made constantly.

324. Smoke Screens. When submarines began to attack shipping, vessels tried to escape by throwing out clouds of dense black smoke. When we studied sulfuric acid, we learned that "oleum" produces a mist that settles slowly and serves as a very effective screen. In Chapter XXVII attention was called to the use of white phosphorus in making dense clouds of phosphoric oxid.

Many other compounds were tried at various times. The tetrachlorids of tin, silicon, and titanium all hydrolyze in moist air and produce hydrogen chlorid. The hydrogen chlorid fumes in moist air because it has so great an affinity for water that it condenses the water vapor into droplets. When ammonia is used with these tetrachlorids finely divided particles of ammonium chlorid are formed.

325. Protective Devices. For making trench helmets manganese steel was used. The steel used in such a helmet must not crack or splinter, it must not indent easily, and it

must be hard enough to prevent a bullet from going through it readily.

Much work was done in an effort to find clothing which



FIG. 134.—Official gas mask. Within a week after the Germans released chlorin gas against the Canadians at Ypres, 2,000,000 simple gas masks were distributed to the French and British soldiers. Then projectiles filled with more dangerous gases were used. The simple masks made from veiling filled with “hypo” crystals were replaced by more efficient masks in which charcoal impregnated with chemicals is used to adsorb or destroy the poison gases. (*U. S. Official.*)

would protect against mustard gas. Oiled clothing was made and used to some extent in the gas factories, but it was never

used at the front. The discomfort from wearing such clothing or from the use of an ointment that was prepared to prevent blisters from mustard gas proved too great an obstacle for field use.

For the lenses of gas masks *triplex* glass was prepared. Such a glass does not splinter when it is struck.

326. Gas Masks. The first gas masks were very crude affairs. As one toxic gas after another made its appearance, the gas mask became more complicated and more efficient. See Fig. 134. The best masks have a canister or box which holds the chemicals needed to adsorb or destroy the gases. Such a canister can be quickly renewed. Various chemicals were used to fill the canisters. *Activated charcoal* alone will adsorb certain gases. To increase its efficiency *soda lime* is usually added. To adsorb or destroy special gases, such chemicals as *sodium phenylate*, *sodium permanganate*, *copper sulfate*, *hexamethyleneamine*, and the *oxids of copper, silver, and cobalt* were employed.

327. Inoculation and Disinfection. Improved methods of sanitation, extensive inoculation against diseases, and marvelous advances in surgery all helped to lower the number of permanent casualties. Serums were used to inoculate the men against typhoid fever, tetanus, and with less success against pneumonia and gas gangrene.

Portable filters were used for purifying drinking water. See Fig. 135. The Lyster bag was also used extensively for the same purpose. This bag contains chlorinated lime for chlorinating the water.

For sterilizing wounds Dakin's solution was used very extensively. It consists of a very dilute solution of sodium hypochlorite of from 0.45 to 0.5% strength. The wound is irrigated with the solution at 2 hour intervals in



FIG. 135.—
Portable filter.
Army type.

such a manner that direct contact with the injured surface is assured.

Other preparations used for sterilizing or dressing wounds include a paste known as "Bipp," which contains bismuth

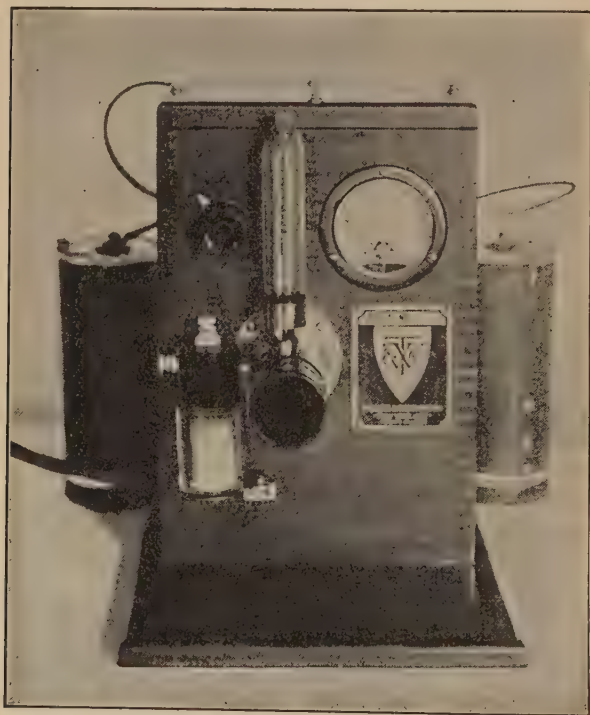


FIG. 136.—Apparatus for administering chlorin.

sub-nitrate, iodoform, and paraffin, and Wright's Hypertonic Solution which contains 5% of sodium chlorid in sterilized water. The former was used by the English for dressing wounds, and the latter for washing wounds to keep them free from infection.

D. WAR CHEMICALS IN PEACE TIME

328. Present Use of War Chemicals. While certain chemicals made so extensively during the war were of little or no value after the armistice was signed, yet many of them were suitable for commercial purposes.

Powder is always in demand by hunters, sportsmen, and for target practice. Other explosives are extensively used for blasting, tunneling, mining, quarrying, blowing out stumps,

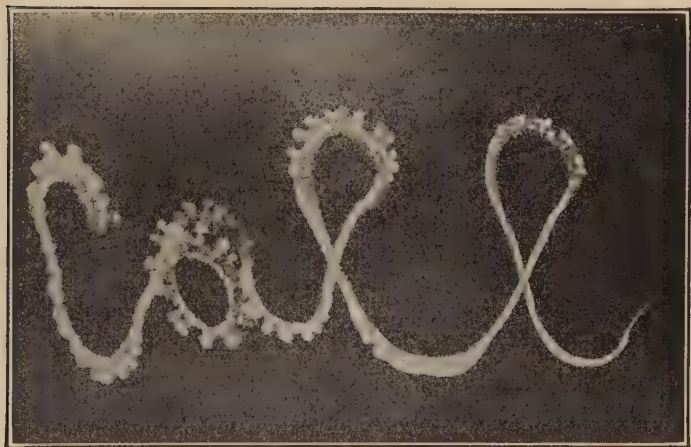


FIG 137.—Writing upon the sky in letters one mile high.

loosening soil, and other industrial purposes. Picric acid finds some use in the dye industry.

Some of the lethal gases are being used to destroy insects. In many of our large cities the police department is equipped with tear gases to be used in case of rioting, or against desperate criminals. It is quite astonishing that chlorin, so deadly when concentrated, is being used in small quantities to alleviate colds and influenza and to sterilize sewage or drinking water. Fig. 136 shows a type of chlorin apparatus that is being used in clinics for treating colds and whooping cough.

Gas masks are valuable to firemen, miners, and workmen in industries where dust, smoke, or poisonous gases are apt to be inhaled.

"Smoke" is being employed to some extent for advertising in what is known as "sky-writing." See Fig. 137. At a height of about 2 miles the pilot writes his message in letters from a half mile to a mile in height. It requires from 6,000,000 to 8,000,000 cu. ft. of "chemical smoke" to form a single letter. The smoke is released as the pilot travels

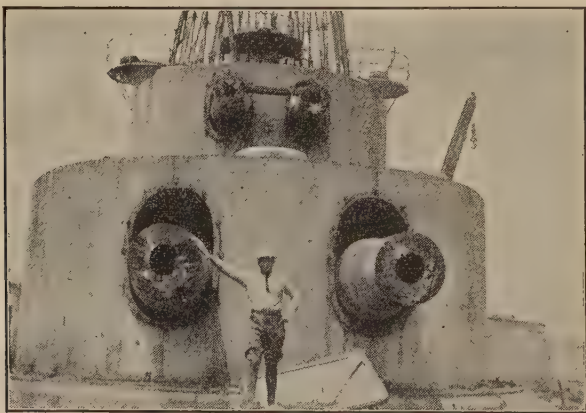


FIG. 138.—Cutting up the guns of a battleship with the oxy-acetylene torch. "Beating shields into plowshares."

from 75 to 120 miles per hour. Some of the battleships and guns are being cut up for use as scrap steel. See Fig. 138.

Every nation will profit by the new disinfectants, improved methods of sanitation, the new serums, and the progress in medicine and surgery that were developed during the war. The same factories that made munitions of war can be used in the manufacture of fertilizers. The chemical plants that were used to turn out hundreds of tons of poisonous gases may with little or no alteration be used to make dyestuffs

and organic chemicals for fighting diseases. Potential alike for peace or war, is it possible to hope that these arsenals may never again be used for making new and more destructive poisons?

QUESTIONS

1. What is meant by a detonator? For what purpose is it used?
2. What advantages does "smokeless powder" have over black gunpowder?
3. Why is modern warfare impossible without a supply of nitric acid?
4. How does dynamite differ from nitroglycerin?
5. Why is chlorine such an important element?
6. What are the objections to the use of white phosphorus for making smoke screens?

CHAPTER XXIX

THE CARBON-SILICON GROUP

329. Introductory. We have already studied the element carbon and its oxids. *Silicon* is an element that is similar in its chemical properties to carbon. Both elements have a valence of 4; their oxids and acids are analogous. While carbon is found free in nature to some extent, silicon is never found native.

A. SILICON AND ITS COMPOUNDS

330. Occurrence. Next to oxygen silicon is the most abundant element. It forms about one-fourth of the earth's crust. A very large number of *silicates* are found, the majority of them being quite complex compounds. *Silica*, SiO_2 , is a very important compound of silicon which occurs in the form of sand and various rocks. The element silicon, which may be obtained by heating sand with carbon in an electric furnace, finds considerable use in the iron and steel industry.

331. Silica. This is one of the most useful compounds of silicon. It occurs in the following forms:

1. *Sand* is the most common form of silica, and it is also one of the most useful. Large quantities of sand are used every year in the manufacture of *glass*. In several ways it is used as an *abrasive*. In the manufacture of sandpaper, a heavy paper is coated with glue, and sand is then sprinkled over the surface. A *sand-blast*, which is used for polishing and cutting very hard surfaces, makes use of a stream of sand driven at a high velocity. *Scouring soaps or powders* usually contain powdered soap, washing soda, and powdered silica, the latter substance being "gritty" enough to do the scouring

work. Sand is also used extensively in making *mortar* and *concrete*, while considerable quantities are used for *lining molds*, into which molten iron is to be poured for making castings. It is especially suitable for this purpose since it is infusible and quite easily removed from the casting after it has solidified.

2. *Sandstone* differs from sand only in that the particles are held together by a kind of cement. Sandstone is used as a building material; it is also sawed into slabs and used for sidewalks or for making grindstones.

3. *Quartz* is a transparent, crystalline variety of silica. Quartz crystals are six-sided prisms surmounted at each end by six-sided pyramids, each crystal having 18 faces (see plate of crystals). While pure *rock crystal* is colorless, traces of impurities impart to it characteristic colors. For example, *amethyst*, *smoky quartz*, *rose quartz*, and *milky quartz* are all well-known varieties of quartz.

Quartz is now melted and fashioned into tubing, crucibles, and other laboratory apparatus. See Fig. 139. Such apparatus is not as easily acted upon by acids and alkalis as ordinary glassware; it has so low a coefficient of expansion that it may be heated red hot and then plunged into cold water without breaking. Quartz is also drawn into very fine threads to be used as suspension fibers in very delicate electrical instruments. A new method of fusing quartz was recently developed by E. R. Berry, of the General Electric Company. Quartz is melted in a graphite crucible in an electric furnace and extruded from the furnace under high pressure. See Fig. 140. It is expected that the price may be decidedly reduced and that quartz utensils will come into much more common use.

4. *Amorphous silica* includes *flint*, *jasper*, *chalcedony*, *sard*, *carnelian*, *onyx*, and *agate*. The last two are made up of bands of different color. Fine specimens of both amorphous and crystalline silica are used as gems.

5. *Silica in Plants and Animals.* Silica is found to considerable extent in plants, especially in the leaves and stems,



FIG. 139.—Silica ware.

where it appears to give rigidity. Silica may replace the fibers of wood and form *petrified wood*.

Some one-celled marine animals have skeletons composed of silica, instead of the ordinary calcium compounds. These animals belong to the order *infusoria*; the *diatoms* are examples. Deposits of *infusorial* or *diatomaceous* earth, consisting of the microscopic remains of these animals, cover

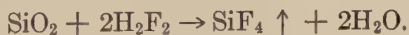
large areas of the ocean bottom as well as extensive land areas. We have already learned that dynamite consists of nitroglycerin absorbed by infusorial earth. This form of



FIG. 140.—Electric furnace from which quartz is extruded.

silica is sold as a silver polish under the name *electro-silicon*. Silica is present in the hair, nails, and horns of animals.

332. Properties of Silica. Pure silicon dioxid can be fused only at very high temperatures. It is insoluble in water and the common acids, with the exception of hydrofluoric acid, which acts upon it as follows:



The silicon tetra-fluorid that is formed is volatile. Alkalies act upon silica more readily than the acids, forming silicates.

333. Silicic Acids. Salts corresponding to several different silicic acids are found in nature. Since silicon has a valence of 4, it may form an acid having the formula H_4SiO_4 . This *orthosilicic* acid forms, when partially dehydrated, *meta-silicic acid*. An acid formed by dehydrating another



FIG. 141.—Electric furnace for making carborundum.

acid in the same series is always called a *meta* acid. Meta-silicic acid is analogous to carbonic acid; since it has the formula H_2SiO_3 . Its relation to ortho-silicic acid is shown by the following equation:



Silica appears to be the anhydrid of this acid, although the acid can not be formed by treating silica with water. The acids of silicon are *very* weak, unimportant compounds but some of their salts are very important.

334. Silicates. The simplest silicates are those of sodium and potassium. They are the only soluble silicates,

their solution being known as *water glass*. Sodium silicate has the formula Na_2SiO_3 . It finds use as a filler in laundry soaps, for making casts and artificial stone, as a binder in making abrasive wheels and furnace linings, for waterproofing wood and cloth, for sizing walls, and as an adhesive in making wall-boards and corrugated paper boards for cartons. When eggs are dipped into a solution of water glass, the pores of the shell are filled by the silicates, and

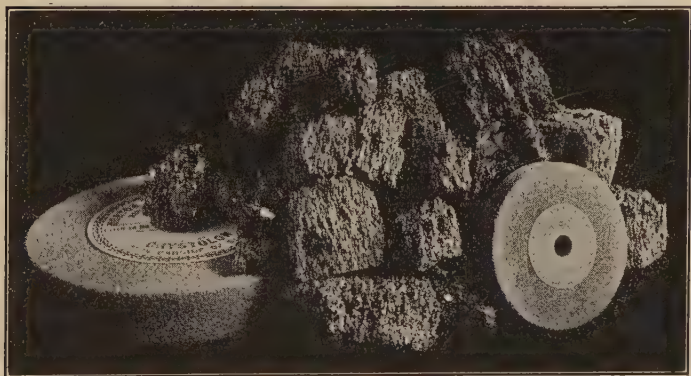


FIG. 142.—Carborundum abrasives.

bacteria can not get through to cause decomposition. Therefore water glass is suitable for preserving eggs.

Silicates that are found in nature include such well-known substances as *clay*, *asbestos*, *talc* or *soapstone*, *feldspar*, *granite*, *garnets*, *slate*, *shale*, and *pumice stone*. Such silicates find extensive use in the cement, pottery, and building industries.

Theoretically, *di-silicic acid* ($\text{H}_8\text{Si}_2\text{O}_8$) and *tri-silicic acid* ($\text{H}_{12}\text{Si}_3\text{O}_{12}$) may exist. Dehydration may occur and it is possible to have silicates containing such radicals as $(\text{SiO}_3)^2$, $(\text{SiO}_4)^4$, $(\text{Si}_2\text{O}_7)^6$, $(\text{Si}_3\text{O}_{11})^{10}$, etc. Furthermore, mixed silicates of different metals are common, thus leading to still greater complexity.

335. Carborundum, CSi , is made by heating sand and coke in an electric furnace. Salt is usually added to make the mixture fuse more easily and sawdust to make it more porous. Fig. 141 shows a commercial electric furnace used for making carborundum. This compound is an extremely hard product that finds use for grinding and polishing metals and other substances. It is made into hones, polishing wheels, and carborundum cloth. Fig. 142 shows specimens of

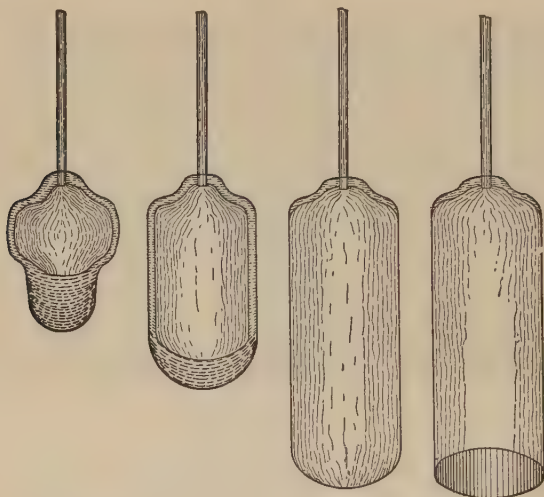


FIG. 143.—Diagrams of the various steps in blowing window glass.

carborundum and the finished wheels. Carborundum abrasives are often sold under the trade name *crystolon*.

B. GLASS MANUFACTURE

336. Glass. In the manufacture of ordinary glass the raw materials, *sand*, *limestone*, and *sodium carbonate*, are heated in a pot of fire clay for about 24 hours. The heating is continued until all the gases are liberated, impurities being

removed by skimming. The product left in the furnace is suited to a wide variety of uses because it has two characteristic properties. It is transparent, and it does not have a sharp melting point, but it softens gradually or becomes plastic when it is heated. Due to its plasticity, it may be rolled, blown, or pressed into any desired shape.

Chemically *glass is made up of the silicates of sodium and calcium*. It is probably a solid solution of these silicates. Potassium is often substituted for the sodium, while lead, barium, aluminum or zinc may take the place of all or part of the calcium.

In making *window glass* the workman introduces into the furnace one end of a blowpipe about 6 ft. long and rolls it around until a sufficient amount of glass adheres to it. See Fig. 143. He then blows a large bubble in this glass and by alternately swinging it, blowing it, and rolling it on a metal plate fashions it into a large cylinder. The ends are then cut off, the cylinder is cut along one side and spread out flat. See Fig. 144. The bulk of the window glass is now

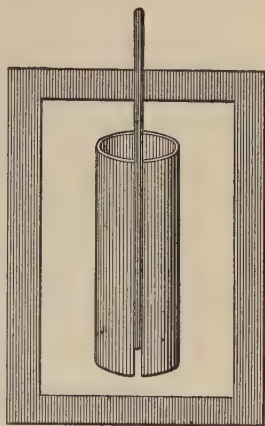


FIG. 144.—Flattening out a cylinder of window glass.

made by machinery. Fig. 145 shows the various steps in blowing small glass articles.

Bottles are blown in molds and then finished by the use of a special tool to shape the neck and round the edge. See Fig. 146. Machines have been made for blowing bottles.

Plate glass is made by pouring the molten glass on a table and rolling it with a metal roller. See Fig. 147. It is then ground with fine sand and polished to make it highly transparent.

Cut glass is molded and then stamped with some design

after which it is cut by means of a wheel. It is afterwards polished with rouge, or iron oxid. Cheap glass

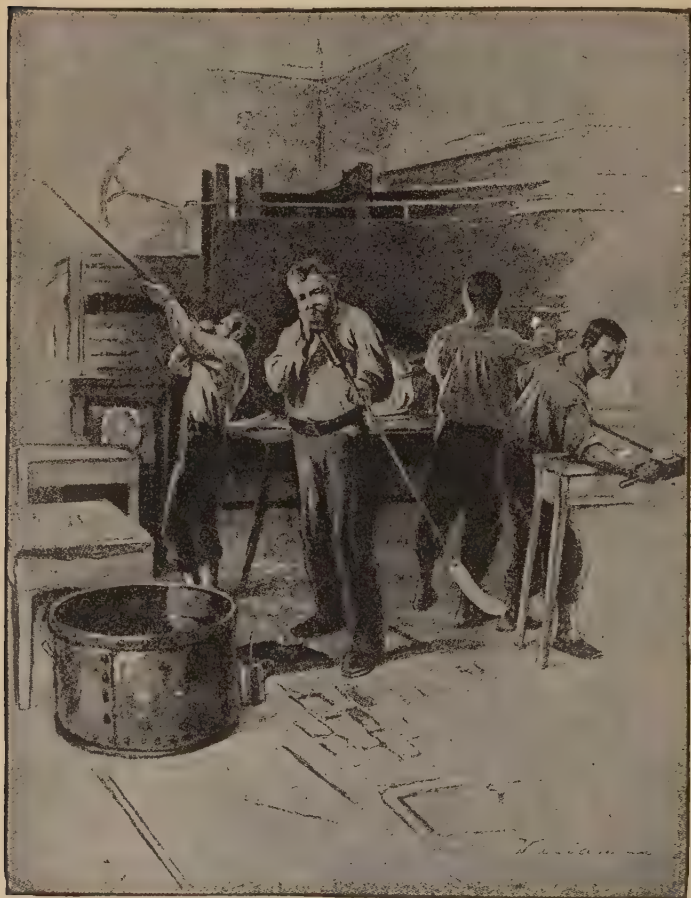


FIG. 145.—Various steps in glass blowing.

dishes are sometimes made by pressing the glass into a mold to impart to the dish the desired design. The

method of drawing glass tubing and rodding is illustrated in Fig. 148.

When glass is cooled quickly it becomes very brittle, and it is apt to break easily. To make glass less brittle it is *annealed* by cooling it slowly. This is accomplished by drawing the glass through a long oven, heated at one end and quite cool at the other. The process is a slow one, requiring in some cases several days.

337. Kinds of Glass. A sodium calcium glass in which the color has been neutralized is known as *crown glass*. When potassium is substituted for the sodium in making glass, the

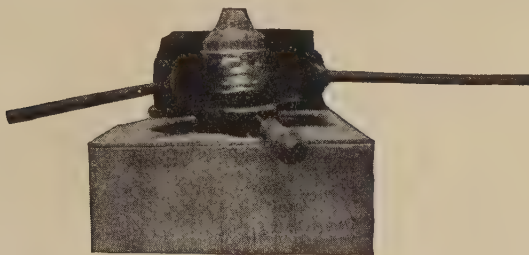
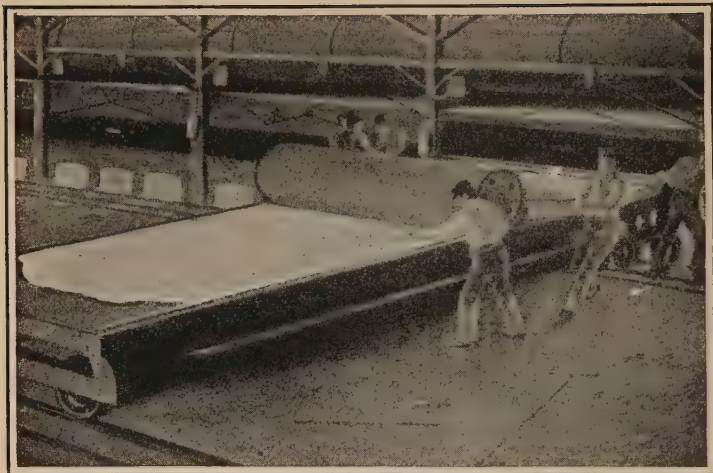


FIG. 146.—Lamp bowl blown in mold.

product is much harder and less easily melted. It is also less readily attacked by alkalis than sodium glass; hence it is sometimes known as “resistance” glass. Prior to the World War the *hard glass*, or *Bohemian glass*, that was used in our laboratories was imported from Germany. Since Germany had practically a monopoly of potassium compounds, our manufacturers were faced with the task of making hard glass without potassium. The problem was soon solved. *Pyrex glass* contains more silica than ordinary glass, and it is made by fusing silica, borax, and aluminum oxid. It is superior to the Bohemian glass in every way. It is hard, not easily fused, resists the action of alkalis, and its coefficient of expansion is lower. Hence laboratory breakage is much less

than formerly. Pyrex glass also finds use in making baking dishes. *Flint glass* contains lead; it is a soft, lustrous glass that has a high index of refraction. Therefore it refracts light more than ordinary glass and gives a better play of colors. It is used in making cut glass, in lenses for optical work, and for making imitation gems. *Wire glass* is made by embedding a network of wire in the glass while it is still



(Permission of Scientific American.)

FIG. 147.—Rolling plate glass.

plastic. *Triplex glass* is made by cementing glass to both sides of a sheet of transparent pyralin. Such a glass will break when struck a sharp blow, but it does not splinter.

338. Color in Glass. Since sand usually contains some iron, ordinary glass is colored slightly green by this impurity. If we look at the edge of a window pane this color may be detected. For high grade glass, the green color is neutralized by the addition of a little manganese. An excess of manganese imparts to the glass a violet or purple color. A trace of chromium in glass gives a clear green color. Selenium is



FIG. 148.—Drawing thermometer tubing.

used to color glass red for signal lights or for automobile tail-lights. Calcium fluorid or cryolite finds use in making opal or white glass. Cobalt gives a blue color and carbon, sulfur, or silver imparts a yellow color.

SUMMARY

The most important elements in the carbon family are *carbon* and *silicon*.

Silica has the formula SiO_2 ; it occurs in nature as sand, sandstone, the several varieties of quartz, amorphous varieties such as flint, agate, and onyx, and to some extent in plants and animals.

Silicates are salts of silicic acid. *Talc*, *mica*, *asbestos*, *granite*, *feldspar*, and *pumice stone* are common silicates found in nature.

Carborundum is a carbid of silicon. It is used as an abrasive.

Glass is a mixture of silicates. The raw materials used in making glass are sand, sodium carbonate, calcium carbonate, potassium carbonate, lead oxid, aluminum oxid, and boric oxid.

Flint glass, crown glass, Bohemian glass, and pyrex are some of the most common varieties. Glass is colored by the addition of metallic oxids to the fused mass.

QUESTIONS

1. Summarize the uses of silicon dioxid or silica.
2. Why is it so difficult to remove the stoppers from ground-glass bottles that are used to contain sodium hydroxid? Would the same difficulty occur if the bottle were used as a container for sodium carbonate solution? Explain.
3. A student in the laboratory heated some sodium carbonate in a silica crucible. The bottom dropped out of the crucible. Explain.
4. How do you account for the small seams seen along the sides of cheap bottles?
5. What are the advantages of "resistance" glass?
6. Why is sand the final product formed by the weathering of the majority of igneous rocks?
7. Glass fruit-jars generally have a greenish tint. Is this color an advantage or a disadvantage?
8. Is a greenish tint desirable for milk bottles? Give a reason for your answer.

9. Tell how ordinary window glass is made. Describe the process of annealing and tell why it is so important.
10. Give the composition of flint glass. What are its properties?
11. How does ordinary glass differ from hard glass in its composition?
12. Why should aqua ammonia never be used for washing cut glass?
13. What are the advantages of pyrex glass for laboratory use?
14. Why does plate glass make better mirrors than ordinary blown glass?
15. For what purposes is "wire-glass" suitable? Triplex glass?

CHAPTER XXX

COLLOIDS

339. Introductory. In Chapter IX we studied the characteristics of the solutions of sugar, salt, etc. Such substances crystallize when they separate from solution and are known as *crystalloids*.

Glue and gelatine *appear* to dissolve in water, but a more careful study shows that they do not form *true* solutions. In a similar manner starch forms a paste with hot water, but it does not really dissolve in water. When the water is expelled again in such cases the substance does *not* crystallize. Substances like starch, glue, gelatin, white of egg, and jelly are known as *colloids*.

340. Colloidal Suspensions. If we stir some fine sand with water we form temporarily a *suspension*. When the agitation stops the sand soon settles. The finer particles settle more slowly. In such a suspension the particles can be seen with a microscope or they may be removed by filtration.

If we examine a drop of salt water under a microscope we can not see any particles at all. The salt does not settle when the solution stands, it can not be removed by filtration, and the salt readily passes through an animal or plant membrane by osmosis. From our study of *true solutions* we know that some of the salt is divided into molecules and that part of the molecules are dissociated into ions.

Colloidal suspensions differ from true solutions and also from ordinary suspensions. They differ from sand in suspension in several ways: 1. *They can not be removed by filtration*, since the particles are small enough to pass through any ordinary filter readily; 2. *They do not settle when the solution*

stands indefinitely; 3. *They can not be seen with a microscope.* Therefore it is obvious that colloidal particles are smaller than those in what we ordinarily think of in suspension.

Colloids in suspension differ from crystalloids in solution in several respects: 1. While a colloidal suspension may appear to be homogeneous and transparent, yet *a beam of light is diffused or scattered in passing through such a suspension* just as it is by the dust particles in a darkened room. A beam of light is not diffused by a true solution. 2. *Colloids have very little effect on the boiling point or freezing point of the suspension.* Thus it appears as if they can not be nearly as numerous as the particles in a solution. 3. *Colloids pass very slowly through a membrane by osmosis.* Crystalloids were separated from colloids by *dialysis* by Graham in 1861. When both colloids and crystalloids are inclosed in a parchment bag and suspended in water, the crystalloids pass through the parchment readily while the colloids are retained. Thus it seems as if colloids in suspension must be made up of particles that are larger than particles in solution. They are probably *aggregates* of molecules; in certain *natural* colloids they may be very large single molecules.

341. Nature of Colloids. When a colloid is dispersed in a liquid it is often spoken of as a solution. Chemists call such solutions *sols*. Frequently a hot *sol* in cooling sets and forms a jelly-like mass known as a *gel*. One of the most familiar examples is the formation of gelatin. Glue is another example. When a *gel* is formed the mass holds a large quantity of water, but the material appears to be solid or semi-solid.

When glue that has formed a *gel* is warmed with water it *reverts* and again forms a *sol*. Such a colloid is *reversible*. When white of egg is heated, it coagulates and forms a *gel*, but it is impossible to form the *sol* phase again. White of egg is an *irreversible* colloid.

That the particles in a *sol* are larger than those in a solu-

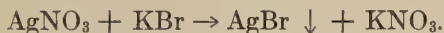
it will remain permanent more or less indefinitely. Similar sols of metals can also be made by using silver, platinum, or copper.

2. A sol may be produced by tritulating or grinding the colloid to a very fine powder. This method is impractical in most cases unless accompanied by other methods.

3. The hydrolysis of a salt very often forms a colloidal sol.

4. Many sols are produced merely by the addition of the dispersing medium. The addition of water to glue or gelatin, of hot water to starch, or of ether to nitro-cellulose are examples. In such true colloids it is probable that the molecules themselves are about the size of the average colloidal particle.

5. If we precipitate silver bromid by double decomposition, we get perfect precipitation when we use the two factors in molar proportions.



By adding a large excess of silver nitrate solution to a solution of potassium bromid, *colloidal* silver bromid is formed.

343. Precipitation of Colloids. We have already seen that one colloid may be precipitated by the addition of another oppositely charged electrically. Colloids are also coagulated by the addition of an acid. The protein in milk is precipitated by the addition of a dilute acid. Sometimes a colloid which is formed in the presence of an acid is precipitated by the use of an alkali. Electricity of high voltage often causes colloids to be precipitated. Some rivers carry considerable material in the form of a colloidal suspension. When it comes into contact with the salt water of the ocean, this silt is precipitated and forms deltas. While the chemist is often interested in precipitating colloids, yet it often happens that he is anxious to stabilize them.

344. Stabilization of Colloids. Since the colloidal particles are all charged with the same sign, the electrical

charges tend to prevent the coalescing of the particles. Sometimes they become covered with a substance which prevents their sticking together. *Tannin* added to finely divided graphite prevents its precipitation. This is used in making aquadag. Gum arabic is used by pharmacists in making emulsions more permanent. Gelatin added to milk has a tendency to prevent curdling. All these substances are known as *protective colloids*. Silver bromid precipitated in

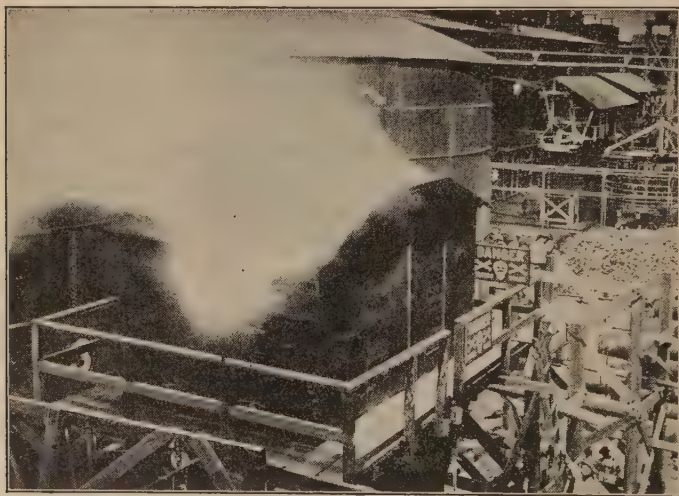


FIG. 151.—Plant fitted with Cottrell precipitator. Note mist when current is off.

the presence of gelatin is colloidal. Use is made of this fact in making the emulsion for photographic films. Gelatin in ice cream makes the cream smoother because a colloid has a tendency to prevent crystallization. For the same reason colloids are added to the electrolyte in many plating baths. Crystalline metals do not adhere well.

345. Kinds of Colloids. While a solid dispersed by a liquid is one of the most common colloids, yet it is possible to

have various other types. In a fog or mist, we have an example of a liquid dispersed by a gas. Conversely, foam is an example of a gas dispersed by a liquid.

Smoke and dust in the air furnish examples of solids in a gaseous medium. Milk is an emulsion in which droplets of one liquid are suspended in another liquid. Mayonnaise dressing is a similar example.

The color in glass is caused by the dispersion of small

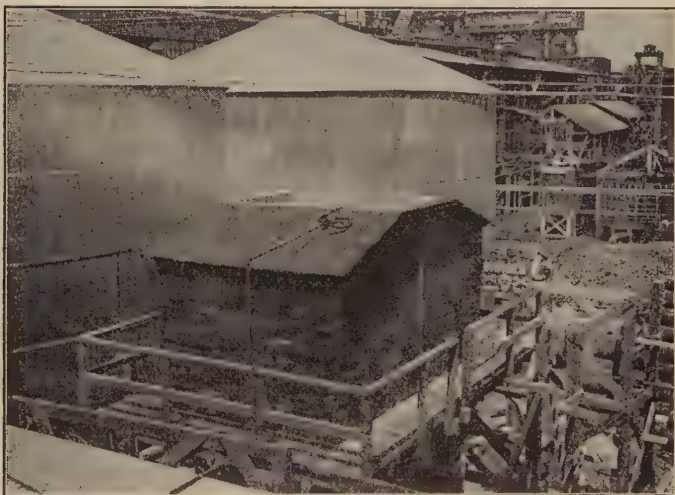


FIG. 152.—Plant fitted with Cottrell precipitator. Mist disappears when current is turned on.

particles of one solid in another solid. A trace of gold or selenium will color a large quantity of glass.

346. Importance of Colloids. Let us refer briefly to a number of important applications of colloids to industrial operations and then discuss two or three of them more fully.

The adhesive properties of glue, mucilage, and varnish are due to their colloidal nature. Paint is a pigment dispersed in an oil medium. The adsorptive property of certain dyes

causes them to stick to the fibers of cloth. Hides contain a colloidal substance which is precipitated by tannin, another colloid, in the making of leather. The strength of cement and asphalt and their ability to resist wear is said to depend upon the fineness of the particles of which they are made.

In the laundry soap emulsifies the fats and oils which hold the dirt, and breaks up the dirt into fine particles. Then it serves as a protective colloid to keep the dirt particles dispersed in the wash water.

Soils may have all the elements needed for plant growth and still not be fertile. An organic colloid known as humus is essential to keep the fine particles of soil from coalescing. Thus the soil can adsorb water which carries the mineral matter to the roots of the growing plant. Salt and alkalis destroy the humus and make the soil sterile.

The sensitized film used in photography consists of an emulsion of silver bromid in gelatin, which serves as a protective colloid. The finished film contains colloidal silver in gelatin.

When 15 c. c. of a concentrated solution of calcium acetate are added to 85 c. c. of alcohol a jelly-like substance is formed. This product is called *solid alcohol*, and finds use as "canned heat." Stearic acid in alcohol produces a similar result.

347. Cottrell Process. Around sulfuric acid plants the acid mist is decidedly annoying. The dust from cement kilns and from the flues of smelters is not only a nuisance, but it is also a waste of useful material.

Cottrell, an American chemist, devised a method of precipitating acid mist and dust particles. Electricity of high voltage is used. The dust particles pass between electrically charged points on wires suspended in the center of the flue and metal plates attached to the walls. Thus they become charged the same as the points and are drawn to the plates and precipitated. Fig. 151 shows the stack of a smelter with the current of a Cottrell precipitator turned off. Fig. 152 shows the effect when the current is on.

348. Firefoam. Water thrown on a fire from burning oil, lacquers, or other light inflammable liquids sinks to the bottom of the container, and the fire continues to burn. See Fig. 153. The carbon dioxid extinguisher shown in Fig. 101 is no more effective because the carbon dioxid escapes rapidly.



FIG. 153.—Diagram to illustrate the principle of smothering fires by the use of foam.

By the use of a colloid to retain the carbon dioxid, thus forming foam or froth, such fires can be smothered.

In the firefoam type of extinguisher alum interacts with the sodium bicarbonate to liberate the carbon dioxid, but licorice or some other colloid prevents the escape of the gas. Thus a blanket of foam several inches thick floats on the burning liquid and shuts off the oxygen supply.

Automobile parts and many other substances are lacquered by immersing them in dipping tanks. The fluid used is highly inflammable. The series of figures 154-7 inclusive show the effects of *foamite* in extinguishing a fire in such a dipping tank.

349. Froth Flotation. Foam or froth is now extensively used to concentrate certain ores, especially those of copper,



FIG. 154.—Fire in a dipping tank.

before the metal is extracted. Very few ores are found pure in nature, but they are generally mixed with some earthy material known as gangue. The principle of froth flotation



FIG. 155.—The firefoam is turned on automatically.

depends upon the fact that certain liquids wet some substances more readily than they do others.

The ore is finely ground and then stirred in a tank of water

to which a little oil is added. The oil adheres to the surface of the ore, but not to that of the gangue. When air is bubbled



FIG. 156.—In a short time the blanket of foam has smothered the fire.

up through the tank, it is adsorbed by the film of oil on the surface of the ore. Thus the air floats the ore to the top of the tank where it is removed, while the gangue settles to the



FIG. 157.—Foam-covered tank after fire is extinguished.

bottom. See Fig. 158. Ores many times as dense as water may be concentrated in this manner, since the ore and oil together form a strong film. It is estimated that 60,000,000

tons of copper ore alone are concentrated by this process annually.

350. Relation of Colloids to Life. A seed falls into the ground, absorbs water, and swells decidedly. The starch, a natural colloid which was stored in the seed, is changed by enzymes into sugar which dissolves and may be readily transported to different parts of the seedling as growth occurs.

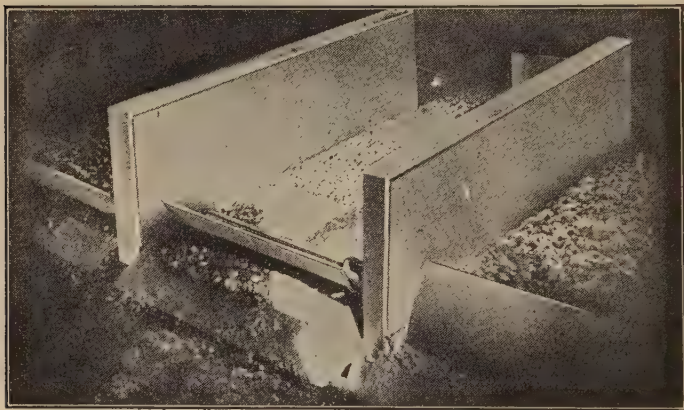


FIG. 158.—Froth-flotation tank for concentrating ores.

The leaves manufacture more starch from carbon dioxide and water, to be stored as food or changed to cellulose or protein.

In the animal body, starch, proteins, and emulsions can not be absorbed directly. They must be changed by enzymes, catalysts used in the digestive process, into smaller particles that are absorbed more rapidly. Then in some mysterious manner protoplasm is formed. With few exceptions the cells are composed almost entirely of colloidal protoplasm. When a cell is pricked or injured it adsorbs water and swelling results. The blood itself is colloidal, as well as the nerve tissues.

SUMMARY

The particles formed when colloids are dispersed are larger than those in a true solution, but smaller than the particles of ordinary suspended matter. They do not settle and they can not pass readily through membranes.

In such *natural colloids* as glue and starch the particles are believed to be large molecules. Other substances not naturally colloidal may be dispersed by the *electric arc*, by *fine grinding*, by *hydrolysis*, or by the use of a *large excess* of one factor during metathesis.

Colloids are precipitated by *oppositely charged colloids*, by *acids* or *alkalis*, by *heat*, and by *electrolytes*. One colloid may protect another.

Colloids are common in many industries. Paint, rubber, varnish, celluloid, asphalt, cement, and the manufacture of leather are examples.

Firefoam, froth flotation, and dust precipitation all depend upon the action of various types of colloidal dispersion. Protoplasm itself, wherever found, is colloidal in its nature.

QUESTIONS

1. How would you test a liquid to determine whether it is a true solution or a sol?
2. What would be the advantage of a perfect protective colloid to a manufacturer of ready-mixed paints?
3. Why is the study of colloids of such great practical value?
4. Gelatin is sometimes added to cow's milk which is to be given to infants. Explain.
5. Does gelatine in ice cream make it more easily digestible?
6. Nitric acid causes the white of an egg to coagulate. Explain.
7. Does alcohol coagulate protein? What effect would you expect strong alcohol to have upon the nervous system?
8. Why does the sting of a bee or the bite of an insect cause swelling?
9. Explain the effect of churning or whipping cream for some time.
10. What is the Cottrell process? In what industries is it used?
11. For what type of fires is firefoam especially suitable? Explain the manner in which it extinguishes a fire.

12. In froth-flotation why do ores six or eight times as dense as water float when the gangue which is usually less than half as heavy as the ore sinks?

13. How does boneblack decolorize sugar solutions?

14. How would you separate sugar from gelatin in water solution?

CHAPTER XXXI

OCCURRENCE AND EXTRACTION OF METALS

A. OCCURRENCE OF METALS

351. Introductory. The elements studied thus far have been largely acid-forming elements. They are the *non-metals*. Of the elements that remain to be studied, all with the exception of boron have base-forming properties. They are called *metals*. It is of interest to inquire how these elements are found in nature. Instead of taking up the occurrence of each metal in detail, thus involving a great deal of pure memory work, an attempt will be made in this chapter to so outline this subject that it may be well covered in a more general way. This plan depends upon a study of the *activity* of the metals, and of the *stability* and *insolubility* of their compounds.

352. Metals Occurring Free. Such inactive metals as gold and platinum do not combine readily with other elements. Thus they are generally found *free* or uncombined in nature. Other metals sometimes found free are silver and copper.

353. Metallic Oxids. Oxygen is so abundant, and it is such an active element, that we would expect to find many metals in nature in combination with oxygen. Such is the case. The most important ores of iron, tin, aluminum, and manganese are oxids. The oxids of copper and zinc are also found to some extent. These oxids are all *insoluble* in water and *stable*. On the other hand, we would hardly expect to find oxids of sodium, potassium, calcium, or barium in nature, since these oxids all interact with water to form soluble hydroxids.

354. Metallic Sulfids. Like oxygen, sulfur is widely distributed and active. With the exception of the sulfids of sodium, potassium, calcium, and barium, which dissolve or hydrolyze in water, *metallic sulfids are stable and insoluble*. Consequently, we find in nature the sulfids of copper, lead, zinc, silver, mercury, nickel, and iron. The sulfids form some of the most important ores of most of these metals.

355. Hydroxids. With the exception of the hydroxids of sodium, potassium, calcium, and barium, metallic hydroxids are generally *insoluble*. We do not find hydroxids in nature so extensively as the sulfids or oxids, because they are less stable. They are apt to lose water and form the oxid, or to combine with hydrogen sulfid to form a stable sulfid, or in some cases with carbon dioxid to form a carbonate. *Hydrated oxids* of iron and aluminum are found in nature and some *basic* (containing hydroxyl radical) carbonates.

356. Carbonates. The carbonates of sodium and potassium are *soluble* in water. Since other carbonates are *insoluble*, we may expect to find many carbonates in nature. The carbonate of calcium is widely distributed. Other carbonates include those of barium, zinc, iron, manganese, and copper.

357. Silicates. In section 334 we learned that all silicates are insoluble except those of sodium and potassium. Many silicates are found abundantly in nature, but they are not satisfactory as ores because they are usually complex and it is very difficult to extract metals from silicates.

358. Sulfates. While the compounds just mentioned are largely insoluble, the sulfates are nearly all soluble. The sulfates of lead and barium are *insoluble*. The sulfates of calcium and silver are *slightly soluble*. Other sulfates are *readily soluble*. Just as we might expect, the insoluble sulfates of lead, calcium, and barium are found in nature.

359. Chlorids. The chlorids of lead, silver, and mercurous mercury are insoluble; other metallic chlorids are

soluble. Contrary to what one might expect, several soluble chlorids occur in nature. They are found in sea-water or in deposits left by the evaporation of land-locked parts of the sea. The chlorids found include those of sodium, potassium, and magnesium. It is interesting to note that all compounds of sodium and potassium are soluble, hence we may expect to find these metals in such stable compounds as chlorids.

360. Nitrates. All nitrates are soluble. Nitrate of sodium is the only nitrate that occurs at all extensively in natural deposits. It is found in the arid regions of Northern Chile.

B. METALLURGY

361. What is Meant by Metallurgy? That science which deals with the methods of extracting metals from their ores is called *metallurgy*. Let us try to distinguish between the terms *mineral* and *ore* as used in metallurgy. *A mineral may be any element or compound occurring naturally in the earth's crust. An ore is a mineral that contains an element in such quantity and form that it may be profitably extracted.* For example, clay and bauxite are both aluminum minerals. Clay is not an ore of aluminum, since the expense of extracting aluminum from clay makes the cost prohibitive. Bauxite is an aluminum mineral that forms the chief ore from which the metal is extracted.

A study of the method of extracting each metal involves a great deal of memory work for the beginner, since the details of the method used depend upon the expense of the operation, the properties of the metal, and the nature of the ore that is being used.

In this chapter, we shall aim to describe and illustrate certain *general* methods of extracting metals from their ores. While certain metals are not obtained by the use of any of these processes, yet one of the processes, or a modification of it, is used in a great majority of cases.

362. Preliminary Treatment of Ores. In the preceding chapter we learned that many ores are concentrated by the froth-flotation process. This is especially satisfactory with low-grade ores, since the bulk of material that goes to the smelter is thus decidedly reduced.

Sulfids, *hydroxids*, and *carbonates* are nearly always converted into oxids before they are smelted. This is accomplished by roasting the ores in the air. The hydroxids lose water, the carbonates lose carbon dioxid, and the sulfur from the sulfids escapes as sulfur dioxid. The following equation is typical:



C. ELECTROLYSIS

363. Electrolysis. We have already had ample proof that the electric current will decompose compounds. Electrolysis is used quite extensively for extracting metals, especially the very active ones. But very few ores are soluble, and the dry ore is a non-conductor; therefore the *fused or melted ore* is generally used. For example, in preparing sodium, the electric current is passed through *melted* sodium chlorid. In this case, the electrolyte is soluble, but when a solution of sodium chlorid is electrolyzed, the sodium attacks the water and forms sodium hydroxid. The same is true of potassium, calcium, and to some extent of magnesium.

Electrolysis is used for the very active metals only, since they are extracted with difficulty by other methods. It is expensive unless very cheap electric power is available. In this country electrical industries flourish at Niagara Falls, making use of the hydro-electric power there developed. Since aluminum is more extensively used than any other metal prepared by electrolysis, we shall illustrate the general method by describing the electrolysis of aluminum oxid.

364. Extraction of Aluminum. In the chemical laboratory of Oberlin College, Professor Jewett made the following

remark: "Any person who discovers a process by which aluminum can be made on a commercial scale will bless humanity and make a fortune for himself." A student, Charles Martin Hall, remarked to a classmate,—“I'm going for that metal.” Two years later Hall handed Professor Jewett a lump of aluminum that he had extracted by the following process:

Bauxite, a hydrated oxide of aluminum, is first dehydrated. Since this oxide is insoluble in *ordinary* reagents and fuses at

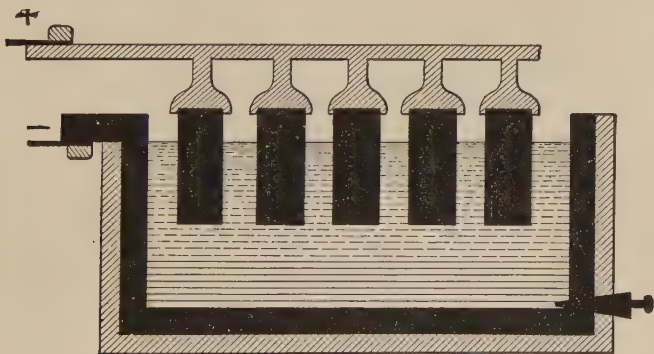


FIG. 159.—Electrolysis of aluminum oxid.

about 2000°C ., Hall began to search for a solvent. He found that cryolite, a fusible mineral that comes from Greenland, readily dissolves aluminum oxide.

An iron box lined with carbon is made the cathode, while rows of carbon rods are used as anodes. The box is kept at a temperature above the melting point of cryolite. When the current is passed, the aluminum oxide is decomposed. Oxygen escapes at the anode and the aluminum sinks to the bottom of the tank where it is drawn off periodically. Fresh aluminum oxide is added from time to time so that the action may be continuous. See Fig. 159.

In 1855 aluminum sold at \$90 per pound. The price in 1870 was \$12 per pound. Hall's process, which was com-

mercialized in 1889, is so successful that the market price of aluminum is now about 20¢ per pound. When Hall died in

1914, he left several million dollars (a part of the estate he acquired through his discovery) to Oberlin College.

D. REDUCTION WITH CARBON

365. Reduction. The reduction of the oxides of metals with carbon is the most important method employed in metallurgy. The reducing agent generally used is *coke*, since it is efficient and not very expensive. Charcoal was employed at one time, and coal is sometimes used. Every year the United States produces about 30,000,000 tons of iron. When we consider that approximately 1 lb. of coke is needed to make 1 lb. of iron, we can understand why there are rows of bee-

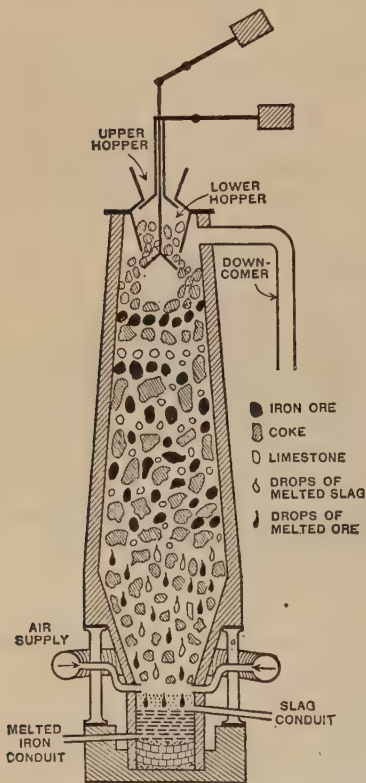


FIG. 160.—Diagram of blast furnace.

hive ovens in Pennsylvania a half mile long. Furthermore, iron is only one of the metals extracted by this method. Copper, tin, and zinc are obtained by reduction. Let us study somewhat in detail the operation of a blast furnace in the preparation of iron as typical of this general method of extracting the useful metals.

366. Use of a Blast Furnace for Extracting Iron. 1. *The furnace used in this operation consists of a steel shell from 80 to 100 ft. high, and from 20 to 25 ft. internal diameter,*

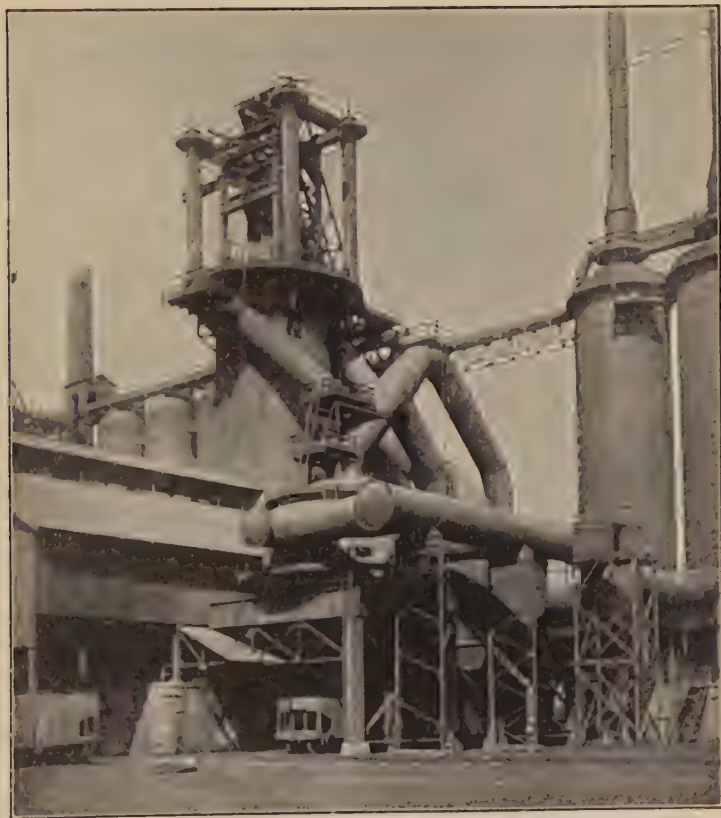


FIG. 161.—A blast furnace for reducing iron ores. The "stoves" seen at either side heat the air for the blast.

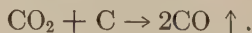
lined with fire brick. See Fig. 160. Water circulates through a shell built into the walls to protect those portions of the furnace subjected to the greatest heat. The heat is due to

the chemical reactions taking place in the furnace. Such action is started by forcing a blast of hot air into the furnace through tuyères. Hence the name *blast furnace*. Fig. 161 shows a blast furnace with the "stoves" that are used for heating the air blast.

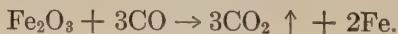
2. *The charge* consists of iron ore in the form of *iron oxid*, *coke*, and a *flux*. Limestone is used as a flux when the gangue in the ore is silica. If the ore contains limestone as an impurity then silica is used as a flux. The charge generally consists of about 3 parts of ore, 2 parts of coke, and 1 part of limestone. Some of the larger furnaces use about 2000 tons of raw material every 24 hours.

3. *The Operation*. The "stoves" contain a checker-work of fire brick which is heated to a high temperature by burning furnace gas in them. Some are being heated while others are in use. Then air is forced through a *pre-heated* stove and conducted into the furnace through the tuyères. Over 50,000 cu. ft. of air at a temperature of from 500 to 800° C. enter a large blast furnace every minute. It takes 4 or 5 tons of air to make a ton of iron.

4. *The Action Inside*. The chemical action is quite complex. The coke is ignited by the hot air blast and some of it burns forming carbon dioxid. But this gas is reduced as it rises and comes into contact with fresh layers of coke above.



The carbon monoxid thus formed reduces the ore as represented by the following equation:



Since the reaction is reversible, it may be driven toward the right only when there is a decided excess of carbon monoxid. See the law of mass action, section 222. For this reason the waste gases removed from the top of the furnace contain from 20 to 30% of carbon monoxid. This *blast furnace gas*

is used as a fuel to operate the entire plant. The white hot liquid iron sinks to the bottom of the furnace where it is drawn off every 4 or 5 hours. It may then be cooled in molds forming pig iron or converted directly into steel.

5. *The flux* serves three purposes: *a.* It unites with the gangue to form a slag which is removed from the furnace by tapping it every 2 hours. The following equation shows how the flux combines with the impurities:



b. The slag that is formed has a lower melting point than the impurities in the ore hence less heat is required. The word *flux* comes from the Latin word *fluere* (to flow), and it is used in chemistry to designate any substance used to lower the melting point of a mixture to which it is added and thus make it more fluid.

c. Since the slag is fairly light it floats on the surface of the iron and protects it from subsequent oxidation which might occur from the air that constantly enters the furnace.

A blast furnace is difficult to start, and when started it is kept in continual operation until it is worn out. A double trap is so arranged at the top that the raw materials may be added without disturbing the operation. The trap prevents the loss of gas. Some furnaces last for 20 years. The large ones make from 500 to 900 tons of iron a day.

E. ALUMINO-THERMICS

367. Introductory. A very active metal may be used to take the oxygen from a less active metal. From the table of heat formation, page 557, we see that 393 large calories of heat are set free during the formation of one mole of aluminum oxid. For example, granular aluminum will take the oxygen from iron oxid if the temperature is raised to a high enough degree to start the reaction.



368. Alumino-thermics. While the use of aluminum to reduce other metals is too costly for general use, yet it is of practical value under certain conditions. 1. It is often used when a small quantity of *carbon-free* metal is needed. Chromium, which is used for making special steels, is sometimes

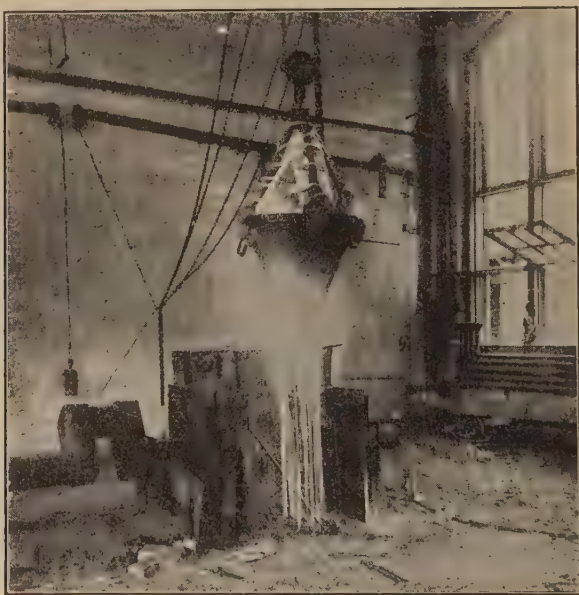


FIG. 162.—Thermit crucible as used for welding.

extracted by this method. Manganese is another metal that is extracted by the use of aluminum. Other metals sometimes reduced by this process include uranium, titanium, molybdenum, and tungsten. 2. Alumino-thermics is sometimes used when the element is too active to be easily reduced with carbon. Silicon and boron are non-metals that are sometimes de-oxidized by the use of granular aluminum.

369. Thermit Welding. While aluminum is too costly to be used for reducing iron oxid, yet the process is used to

produce iron for welding purposes. The following method of *autogenous* welding was devised by Dr. Hans Goldschmidt. A mixture of granular aluminum and iron oxid, known as *thermit*, is placed in a crucible over the metals to be welded. An igniting mixture, consisting of barium peroxid and powdered aluminum or magnesium, is placed on top of the thermit to start the reaction. See Fig. 162. The chemical action is as follows:



As the white hot molten iron is reduced it runs down over the broken ends and literally fuses them together to form a



FIG. 163.—The completed weld made by the use of thermit as in Fig. 162.

solid piece. See Fig. 163. *Black* thermit is a mixture of black oxid of iron, Fe_3O_4 , and granular aluminum. The temperature produced by the reaction is estimated at about 3500°C . It is interesting to note that thermit bombs were made during the World War and used for incendiary purposes.

F. REPLACEMENT

370. One Metal may Replace Another. If we suspend a strip of copper in a solution of silver nitrate, the copper gradually goes into solution and the silver is precipitated.



Use is sometimes made of the fact that one metal will replace another. In the metallurgy of silver, the above process is used. Scrap iron is used to precipitate the copper from waste waters in the copper industry. Iron may also be used in the precipitation of gold and silver. In the following section a replacement table is given from which it is possible to determine not only the order of replacement, but also several other interesting facts concerning metals.

371. Replacement Series. The position of any metal in the adjoining table depends upon its relative tendency to

REPLACEMENT SERIES

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Iron
Cobalt
Nickel
Tin
Lead
HYDROGEN
Copper
Mercury
Silver
Platinum
Gold

ionize. Potassium enters the ionic condition more readily than other metals; for that reason it stands first in the replacement series. Since potassium ionizes more readily than iron, it will replace iron from solutions of iron compounds. For the same reason iron replaces copper, silver, or gold. In short, *an element will replace any element that stands below it in the replacement series; it will be replaced from its compounds by any element standing above it in the table.*

The farther apart any two elements stand in the series, the greater the potential difference produced by those two metals when used to make a voltaic cell. For that reason this series is sometimes called

the *electromotive series*. To illustrate, copper and zinc may produce an electromotive force of 1.1 volts; copper and iron give only 0.67 volt; but silver and aluminum furnish more than 2 volts.

The elements that stand above hydrogen in the series are not found free in nature, while those below hydrogen are frequently found uncombined. Hydrogen chlorid does not act on any of the metals below hydrogen, since these metals do not replace hydrogen from its compounds. The metals below hydrogen may be acted upon by such strong oxidizing acids as nitric and sulfuric, but hydrogen is not liberated. An oxid is first formed which is then converted into a salt of the acid and water by the subsequent action of the acid.

The metals that stand above zinc can not be reduced by hydrogen alone. Those that stand above manganese are prepared by electrolysis. They are the most active metals, being readily acted upon by acids, water, and oxygen, with the exception of aluminum. The metals that fall below copper do not tarnish in air. Their oxids are easily decomposed by heating. Since water contains some hydrogen ions, most of the metals that stand above hydrogen in the series interact with water, or *rust* when exposed to moisture.

SUMMARY

All oxids, sulfids, and hydroxids are insoluble except those of sodium, potassium, calcium and barium, and of these the oxids and sulfids generally unite chemically with water.

All ordinary carbonates are insoluble except the carbonates of sodium and potassium.

The sulfates of barium, strontium, and lead are insoluble; the sulfates of silver and calcium are slightly soluble; all other sulfates are soluble.

The chlorids of lead, silver, and mercurous mercury are insoluble; other chlorids are soluble.

All nitrates are soluble.

The minerals and ores found most abundantly in nature are oxids, sulfids, carbonates, and silicates. We may expect to find in nature:

1. *Inactive metals occurring uncombined.*
2. *Sulfids, oxids, and carbonates of the heavy metals (Berthollet's laws of insolubility).*
3. Those soluble compounds of *active* metals that are *very stable*.

Metallurgy is the science that deals with the extraction of metals from their ores.

With few exceptions, metals are extracted by one of the following methods: *electrolysis; reduction; aluminothermy; replacement*. The light metals are generally extracted by electrolysis. The common heavy metals are extracted by reducing their ores with carbon. Metals less widely used and the more valuable metals are extracted by aluminothermy or by replacement with a cheaper metal.

QUESTIONS

1. The only soluble silicates are those of sodium and potassium. Would you expect to find silicates widely distributed in nature?
2. Why are the metals that stand above hydrogen not found free in nature?
3. From the position of mercury in the replacement series, what do you think would be the effect of heating cinnabar, or mercuric sulfid?
4. Which metal do you think would be more easily reduced, iron or copper? Iron or aluminum?
5. Why is it necessary to fuse the ore before extracting metals by electrolysis?
6. Distinguish between metal, mineral, and ore.
7. State the advantages and disadvantages of extracting metals by electrolysis.
8. What is the chief objection to the use of aluminothermy in metallurgy?
9. What is meant by the term "flux" as used in metallurgy? State its uses in extracting iron.
10. Summarize the facts that may be observed by a careful study of the replacement series of metals.

CHAPTER XXXII

ALKALI METALS

372. The Sodium Family. Sodium and potassium are the most important metals in this family. They were discovered by Sir Humphrey Davy early in the nineteenth century. They are often called the *alkali metals*, since their hydroxids are strongly alkaline. The valence of all the elements in this family is one. The metals are strongly electropositive. All ordinary compounds of these metals are soluble in water. Sodium and potassium occur in nature as chlorids, the former being very widely distributed. Potassium chlorid and also the sulfate are found at Stassfurt, Germany, associated with compounds of calcium and magnesium. The Stassfurt deposits are remarkable. They occur in beds several hundred feet thick. The metals in this group are all isolated by electrolysis of the *fused chlorids*. The ammonium radical forms salts which are similar to those of sodium and potassium. Thus the ammonium compounds are included in this chapter.

A. SODIUM

373. Properties of the Metal. Sodium is a silver white metal, so light that it floats on water. It is so soft that it may be molded like wax. Chemically it is one of the most active metals. It unites with oxygen so readily that it must be kept in oil to prevent oxidation. It also unites chemically with most non-metals; it interacts with water and with all ordinary acids. Sodium forms some of the most important chemical compounds known to chemistry. The metal finds some use as a reducing agent. Used as a

catalytic agent it converts *isoprene*, a hydrocarbon having the formula C_5H_8 , into artificial rubber.

374. Sodium Chlorid. $NaCl$. Sodium chlorid, or common table salt, occurs in nature in sea-water, in salt-wells, and in rock deposits. Rock salt is mined in some localities, but most of the salt of commerce is obtained by the evaporation of natural brines, either by the use of natural or artificial heat. In this country, New York, Michigan, Ohio, Kansas, and a few other States are large salt-producers.



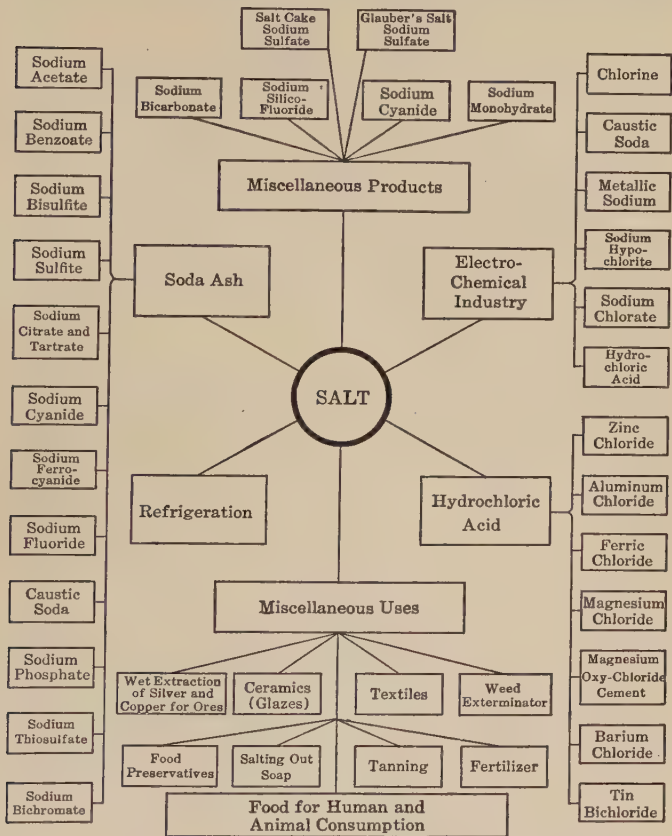
(Permission of Scientific American.)

FIG. 164.—Harvesting salt from San Francisco Bay.

The United States produces more than 30,000,000 barrels annually. Sodium chlorid crystallizes in cubes. Pure salt is not deliquescent, but magnesium chlorid, a very deliquescent compound, is usually present as an impurity. This accounts for the fact that salt becomes wet and “packs” in moist weather. See Fig. 164.

Sodium chlorid, as the cheapest compound of sodium, is used as a starting point in the manufacture of all sodium compounds and also of all compounds containing chlorin. Thousands of tons of salt are used every year as a pre-

servative, in packing and curing meats. Mixed with snow and ice, salt forms a good freezing mixture. It is estimated



(Courtesy of International Salt Co.)

FIG. 165.—Chart showing the varied uses of salt.

that the average American uses about 11 lb. of salt a year in seasoning his food. Considerable quantities are fed to sheep and cattle. The chart, Fig. 165, shows the important part that salt plays in the industries.

375. Sodium Nitrate. NaNO_3 . Extensive beds of sodium nitrate are found in Western South America, especially in the desert regions of Northern Chile. It is a colorless, crystalline compound, slightly hygroscopic. Large quantities of sodium nitrate are used for fertilizers. Since it is the only nitrate found to any considerable extent in nature, it is used for making nitric acid and other nitrates. Since it adsorbs water, it is not suitable for making gunpowder.

376. Sodium Sulfate. Na_2SO_4 . Sodium sulfate, a by-product from the manufacture of hydrochloric acid, is used in making glass and sodium carbonate. It forms colorless crystals, having the formula $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, used in medicine under the name Glauber's salt.

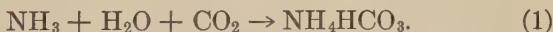
377. Sodium Hydroxid. NaOH . In the chapter on bases we learned that sodium interacts with water to form sodium hydroxid. This compound is produced commercially by the electrolysis of a solution of sodium chlorid, the electrodes being in separate compartments so that the chlorine which is liberated at the anode does not by any chance come into contact with the hydrogen or the sodium hydroxid at the cathode. Much of the sodium hydroxid is now made in Nelson cells as described in section 254. Sodium hydroxid is a white, crystalline solid. In purified form it is often cast in sticks. It is deliquescent, taking on first water from the air and then carbon dioxid, changing slowly into the carbonate. In water solution it forms one of the strongest known bases. Since it attacks the flesh and skin it is known as *caustic soda*. Its most important use is in making soap. For household use, such as cleaning sinks, it is known as *lye*.

378. Carbonates of Sodium. Both carbonates of sodium are very important compounds. *Sodium carbonate* has the formula Na_2CO_3 . *Sodium bi-carbonate*, commonly called soda, has the formula NaHCO_3 . LeBlanc won a prize offered by the French government to any one who could make the carbonates of sodium commercially by starting

with common salt. The LeBlanc process is still used in France. In the United States these carbonates are made by the Solvay process.

Solvay Process. This process was devised by Ernest Solvay, a Belgian. No commercial operation is of more interest to the student in showing how by-products can be utilized. In a large plant at Solvay, New York, the raw materials used are *salt, limestone, and coal*. The Solvay company operates its own gas plant. They utilize the gas and coke for fuel. The ammonia which is obtained as a by-product is used in making the carbonates of sodium. The salt water is pumped to the plant from near-by wells. Limestone is quarried in the vicinity of Solvay. It is heated to supply the necessary carbon dioxid.

Under proper conditions of temperature and pressure a *saturated solution of sodium chlorid is treated with ammonia and carbon dioxid*. The ammonia dissolves in the water and combines with the carbon dioxid to form ammonium bicarbonate:



The sodium chlorid interacts with the ammonium bicarbonate forming the bicarbonate of soda:



If sodium carbonate is to be prepared the sodium bicarbonate is heated:



When the limestone is heated to supply the carbon dioxid, calcium oxid is produced at the same time.



It is slaked by the addition of water,



and the slaked lime is heated with the ammonium chlorid obtained as a by-product from the gas plant and also with that left in forming the sodium bicarbonate as shown in equation (2):



Thus the ammonia is used over and over again. The carbon dioxid from equation (3) is also utilized. In fact all the products are either used over again in the process or marketed as by-products. The calcium chlorid which remains after the recovery of the ammonia is a dehydrating agent. It is used as a binder on some dirt roads to prevent the accumulation of dust.

Leblanc Process. This process is older than the Solvay process and more expensive. It is still used because several valuable by-products are obtained. Sodium chlorid is treated with sulfuric acid to form sodium sulfate and hydrogen chlorid. At a low temperature the bi-sulfate is formed as represented by the first equation and at a red heat the bi-sulfate unites with sodium chlorid forming sodium sulfate.



The sodium sulfate is then reduced to sodium sulfid by heating it with carbon:



When sodium sulfid is heated with calcium carbonate, sodium carbonate and calcium sulfid are produced:



The calcium sulfid is converted into sulfur and bleaching powder, which form valuable by-products. The most

important by-product, however, is the hydrochloric acid prepared as shown in equation (a).

Sodium carbonate forms colorless crystals having the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. It is used extensively in the manufacture of glass. It hydrolyzes to some extent in water forming a basic solution. For this reason it is used in laundries under the name of *washing soda*. This carbonate is also used to soften hard waters.

Sodium bicarbonate is generally known as *baking soda*. It interacts with acids or acid salts liberating carbon dioxide which we have learned is a leavening agent. With the lactic acid in sour milk it interacts to form sodium lactate, water, and carbon dioxide. Hence the use of sour milk with baking soda as a leavening agent.

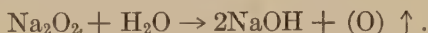
For use with water or sweet milk baking powder is used. All baking powders contain *sodium bicarbonate* which supplies the carbon dioxide. There are three common types of baking powder: (1) *Cream of tartar*, (2) *Acid phosphate*, (3) *Alum*.

In the first type of powder mentioned cream of tartar, $\text{KHC}_4\text{H}_4\text{O}_6$, which is an *acid* salt, is used to liberate the carbon dioxide. Such powders sometimes contain tartaric acid. In the second type of powder, an acid salt such as calcium acid phosphate or sodium acid phosphate is added to free the gas from the soda. Alum is not an acid nor an acid salt, but it hydrolyzes in water and acts as an acid.

Considerable discussion has arisen concerning the healthfulness of baking powders containing alum. From investigations carried on by the research laboratories in Washington, there was no evidence of any harmful results from the use of alum powders. Such powders were manufactured for the use of the United States Commissary Department during the World War. Starch is used in all baking powders to keep the powder dry, since deterioration occurs in the presence of moist air. Not more than 20% is needed, and a larger

percentage should be considered an adulterant. As high as 50% has been added by some manufacturers.

379. Sodium Peroxid. Na_2O_2 . When sodium is burned in the air a yellowish-white powder is formed; it is peroxid of sodium. This peroxid unites with water to form sodium hydroxid while oxygen is set free.



Since nascent oxygen is liberated in this reaction such a solution forms an excellent bleaching agent. Because fibers bleach more readily in an alkaline solution, sodium peroxid is taking the place of hydrogen peroxid to a considerable degree as a bleaching agent. To be used for preparing oxygen, sodium peroxid is sold under the name *oxone*.

380. Sodium Thiosulfate. $\text{Na}_2\text{S}_2\text{O}_3$. This compound is commonly called "hypo." It is used in photography as a fixer to dissolve the unchanged silver salt that has not been reduced by the action of the light and the developer. It is also used as an "antichlor."

381. Sodium Cyanid. NaCN . This compound of sodium is a white crystalline solid. *It is extremely poisonous and must be handled with great care.* With acids it sets free the *deadly poisonous hydrocyanic acid*, commonly called *prussic acid*. Sodium cyanid is used in the metallurgy of gold, in plating with silver and gold, and in the case-hardening of steel.

B. POTASSIUM

382. Introductory. The compounds of potassium resemble those of sodium so closely, that they are often used interchangeably. Potassium compounds are rather more easily soluble and they have been extensively used in the laboratory. When the shortage of potassium compounds occurred during the war, sodium compounds were found quite as satisfactory in most cases. The use of sodium compounds

has continued, since they are cheaper and "go farther." The atomic weight of sodium is 23, and that of potassium is 39. Therefore we must use 56 lb. of KOH to get 17 lb. of hydroxyl (OH), while we can get an equal amount of hydroxyl from 40 lb. of sodium hydroxid.

383. Potassium. Potassium is obtained by the electrolysis of *fused* potassium chlorid. It is a soft, bluish-white metal that resembles sodium quite closely. Potassium floats on water. It must be kept in oil, since oxygen attacks it readily. Potassium decomposes water even more energetically than sodium does.

384. Potassium Chlorid. KCl. The deposits at Stassfurt, Germany, are important sources of potassium compounds. The chlorid and sulfate are found here in beds several hundred feet thick. Prior to the World War Germany had a monopoly of potassium compounds, but beds of potassium compounds occur in Alsace, which is now a part of France. Potassium chlorid is the starting point for nearly all potassium compounds. It furnishes the bulk of the "potash" which is used in commercial fertilizers.

385. Potassium Nitrate. KNO_3 . This compound is made by mixing hot concentrated solutions of sodium nitrate and potassium chlorid. We would expect the action to be reversible,



but sodium chlorid, being less soluble than the other compounds in hot water, separates first as crystals. Potassium nitrate when mixed with sulfur and powdered charcoal forms black gunpowder. It is also used to some extent for curing meats, especially corned beef. Chopped meats retain their bright red color when sprinkled over with a little potassium nitrate.

386. Potassium Hydroxid. KOH. The method of making potassium hydroxid is analogous to that of preparing

sodium hydroxid. It resembles the hydroxid of sodium in both physical and chemical properties. In fact they are so much alike that usually one may be substituted for the other. Since the hydroxid of sodium is much cheaper, potassium hydroxid is not very extensively used. It finds use in the soap industry and as the electrolyte for the Edison storage battery.

387. Potassium Carbonate. K_2CO_3 . *Potassium carbonate* is present in wood ashes. Wool perspiration, or suint, also contains potassium carbonate which is now recovered from the waters used in washing wool. Considerable potassium carbonate is present in the mother liquor left after sugar crystals have been obtained from sugar beets. These illustrations show the important relation of potassium compounds to plant and animal life. The most important use for potassium carbonate is in the manufacture of hard glass.

388. Potassium Chlorate. $KClO_3$. When the halogens are introduced into a solution of an alkaline hydroxid two reactions may occur. If the solution of the hydroxid is cold and dilute, a reaction like the following occurs:



Both the *hypochlorite* and the *chlorid of potassium* are formed. If the solution of the hydroxid is hot and concentrated an entirely different reaction takes place:



The latter reaction is made use of in the manufacture of *chlorates*. Potassium chlorate is a white crystalline solid. It is a very vigorous oxidizing agent, hence it finds considerable use in the manufacture of matches, explosives, and fireworks. Chlorate of potash tablets are used for sore throat.

389. Other Potassium Compounds. Both *potassium*

bromid, KBr, and *potassium iodid*, KI, are used in medicine and in photography. *Potassium acid carbonate*, KHCO_3 , was formerly used for baking under the name *saleratus*.

C. AMMONIUM COMPOUNDS

390. Ammonium Chlorid. NH_4Cl . Ammonia and hydrogen chlorid combine to form *ammonium chlorid*, a white crystalline salt. The reaction is reversible, depending upon the temperature.



This salt is often called *sal ammoniac*; it is used in voltaic cells, as a flux in soldering, and to some extent in medicine.

391. Ammonium Nitrate. NH_4NO_3 . We have already learned that this compound is used to prepare nitrous oxid, or laughing gas. It is also used to prepare "safety explosives" for use in mines. Marsh gas, which is often liberated in coal mines, forms an explosive mixture with air. Most explosives used for blasting will ignite this mixture of marsh gas and air, but ammonium nitrate mixed with rosin or sulfur forms an explosive which does not usually generate enough heat when it explodes to ignite the marsh-gas mixture. It is also mixed with T. N. T. for use as an explosive.

392. Other Ammonium Compounds. *Ammonium hydroxid*, NH_4OH , was discussed in Chapter XVII. *Ammonium sulfate* $(\text{NH}_4)_2\text{SO}_4$, is a by-product obtained in the manufacture of coal gas. It is used as a fertilizer. *Ammonium sulfid* $(\text{NH}_4)_2\text{S}$, is a liquid made by passing hydrogen sulfid into a solution of ammonium hydroxid. This solution is used as a reagent in qualitative analysis. *Ammonium carbonate* $(\text{NH}_4)_2\text{CO}_3$, is a white solid that slowly decomposes to form the acid carbonate and ammonia. It finds use as a laboratory reagent, for smelling salts, and in making aromatic spirits of ammonia.

D. FLAME TESTS

393. Flame Tests. Several metals when heated high enough to be volatile burn with a characteristic flame. This furnishes an excellent means of identifying them. The test is made as follows: A platinum wire is held in the flame until it is clean or until it imparts no color to the flame. It is then dipped into the salt or solution to be identified and again held in the flame. *Sodium* imparts an intense yellow color to the flame; the *potassium* flame is violet; *lithium* and its compounds give a crimson flame; *barium* compounds give a yellowish-green flame. Unfortunately this simple test is often obscured by the presence of other compounds; a spectroscope is then necessary to distinguish one element from others that may also be present.

394. Use of the Spectroscope. When rays of sunlight are passed through a triangular prism, a band of colors called a *spectrum* is produced. A white hot platinum wire produces a band of colors when its rays fall upon a prism. If we examine burning sodium through a spectroscope, which is an instrument for producing and examining spectra, we find that it gives a bright yellow band. This band is always formed in the same relative place in the spectrum so that it serves to identify sodium. Potassium produces both red and violet lines. From the Spectrum Chart used as the frontispiece, we see the characteristic colors of hydrogen, nitrogen, and carbon. The stars and other heavenly bodies give characteristic spectra by means of which it is possible to determine the elements of which they are composed. The method of spectrum analysis is the result of the work of two German chemists, Bunsen and Kirchoff.

SUMMARY

The alkali metals are prepared by the electrolysis of their *fused* chlorids. Their hydroxids are prepared by the electrolysis of *solutions* of their chlorids. These hydroxids are very strong bases.

The chlorids of sodium and potassium occur in nature. They are used in preparing other sodium and potassium compounds. *Potassium chlorid* is an important fertilizer.

Sodium nitrate is used as a fertilizer; it is also used for making nitric acid and in the preparation of potassium nitrate which is used in the manufacture of black gunpowder.

The *carbonates* of both *sodium* and *potassium* are used in the glass industry. Sodium carbonate is known as *washing soda*; sodium bicarbonate is used as *baking soda*, and as an essential constituent in baking powders.

Sodium peroxid is an important *oxidizing agent* used in the bleaching industry.

Potassium chlorate is made by passing chlorine into a hot concentrated solution of potassium hydroxid. It is used as an oxidizing agent in matches, fireworks, and explosives.

Ammonium salts are similar in many respects to the salts of sodium and potassium. The chlorid, sulfid, sulfate, and nitrate are the most important salts. Ammonium hydroxid is an active base although much weaker than sodium or potassium hydroxid.

Some metals impart to a flame a characteristic color by which they can be identified. Sodium gives an intense yellow flame; potassium, a violet flame.

QUESTIONS

1. Why are sodium compounds so important in chemistry?
2. Discuss the industrial importance of sodium chlorid.
3. Why are water solutions of sodium carbonate and sodium bicarbonate alkaline? Which would you expect to be more strongly alkaline?
4. How could you distinguish sodium nitrate from potassium nitrate? Sodium chlorid from sodium nitrate?
5. If sold at the same price per pound, which would be the cheaper leavening agent, sodium acid carbonate or potassium acid carbonate?
6. In what laboratory exercises have the following compounds been used: sodium chlorid, sodium nitrate, potassium chlorate, sodium carbonate, ammonium chlorid, ammonium nitrate?
7. What uses can be made of sodium peroxid?
8. What methods are in use to keep salt from "caking"?
9. Washing soda dissolves wool and turns oak floors black. Under what circumstance may it be used as a cleansing agent?

10. In what ways did this country feel the effects of the "potash famine" during the early period of the World War?

11. What properties does a solution formed by passing water slowly through wood ashes have? What name is given to this solution? What is its use?

12. How would you prepare sodium bromid? Potassium iodid?

13. If a manufacturer uses sodium carbonate in quantity, what advantage would it be for him to buy calcined (heated strongly) sodium carbonate?

14. Why does the use of baking powder as a leavening agent give more consistent results than the use of sour milk and soda?

PROBLEMS

1. How many pounds of nitric acid can be made from 100 lb. of potassium nitrate that has a purity of 85%?

2. How many grams of hydrochloric acid can be neutralized by 10 gm. of sodium hydroxid? How many grams of the same acid would 10 gm. of potassium hydroxid neutralize?

3. If crystallized sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, sells for 10¢ per pound and sodium carbonate that has effloresced in air until its formula is $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ sells for 16¢ per pound, find the cost in each case of one pound of anhydrous sodium carbonate.

CHAPTER XXXIII

ALKALINE EARTH GROUP

395. General Family Characteristics. This family consists of three elements: *calcium*, *barium*, and *strontium*. Like the alkali metals these elements may be prepared by electrolysis, but since they have little practical application, the demand is small. They interact with water but not so rapidly as the alkali metals. Their hydroxids form strong bases, hence this family is sometimes called the "alkaline earth group." Calcium, barium, and strontium have a valence of 2. They are never found free in nature.

A. CALCIUM

396. Calcium Carbonate. CaCO_3 . One of the most abundant compounds of calcium is the carbonate. It is also one of the most useful.

Limestone is one of the important forms. Although pure calcium carbonate is white in color or colorless when crystalline, the natural deposits are



FIG. 166.—Marble quarry several hundred feet deep.

usually colored by the presence of organic matter or iron compounds. It is used as building stone, especially for foundation work. Enormous quantities are heated to produce quicklime. With or without cement crushed limestone is extensively used for making and repairing roads. Tons of limestone are used every year as a flux in the reduction of metals, espe-

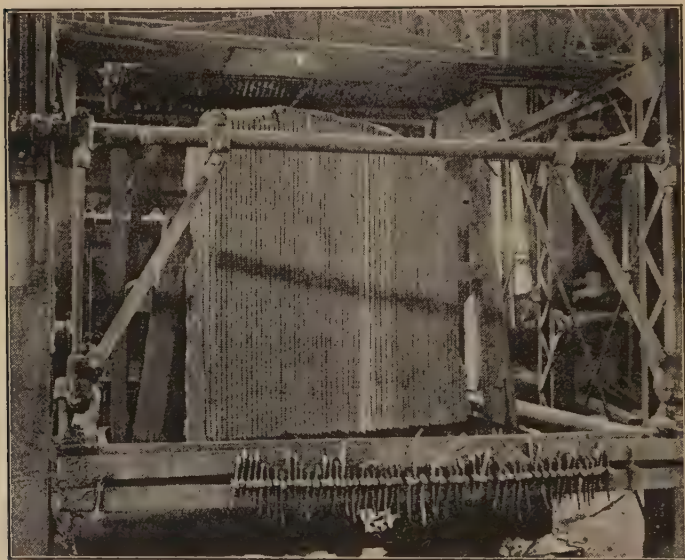


FIG. 167.—Sawing marble with smooth metal bands.

cially iron. We have already learned that it is used in the making of soda, glass, and carbon dioxid.

Calcite is a crystalline variety of calcium carbonate. Transparent colorless specimens are known as *Iceland spar*. They exhibit the property of double refraction of light.

Marble consists of fine grains of calcite. By subjection to natural heat and pressure, limestone is changed into marble. Since it takes a high polish and is easy to cut, marble is used for statuary, monuments, and as a finishing

stone. Marble is cut from the quarries with channeling machines into blocks that weigh about 15 tons. See Fig. 166. These blocks are hoisted and sawed with smooth iron bands, set in a moving horizontal frame. Water carrying particles of sand flows down over the block as the smooth iron bands are drawn back and forth. These particles of sand serve as teeth for the saws. See Fig. 167. In some cases circular saws

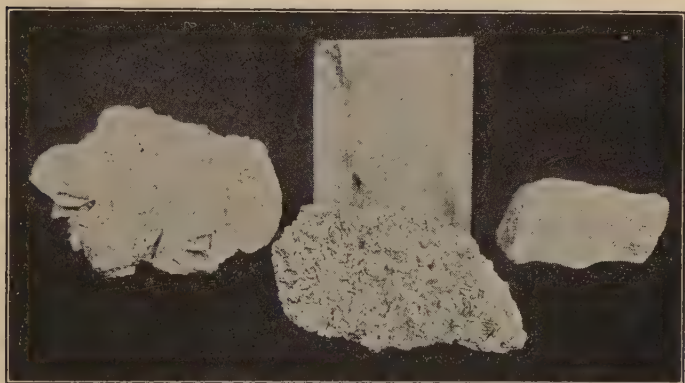
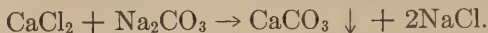


FIG. 168.—Varieties of calcium carbonate, including a slab of polished marble, fossil-bearing limestone (left), oölite (right), and coquina (center).

set with diamond teeth are used. The slabs are rubbed with sand and water and then highly polished. The quarries at West Rutland, Vermont, are over 300 ft. deep and have a total underground floor space of 17 acres. Marble occurs in many different colors.

The shells of such animals as clams, snails, and oysters consist largely of calcium carbonate. In past geologic ages, shell deposits from such animals became firmly cemented together forming large masses of solid rock. Old Fort Marion, at St. Augustine, Florida, is built of a shell rock called *coquina*. See Fig. 168. *Chalk* is of geologic formation, consisting of the microscopic remains of small marine animals.

Precipitated chalk is an artificial calcium carbonate prepared by the action of calcium chlorid on sodium carbonate.



It is soft and finely divided, forming a non-gritty scouring powder, suitable for tooth powders.

397. Caves. Limestone caves occur in the earth's crust due to the solubility of calcium carbonate in a water solution of carbon dioxid. The carbonate, while insoluble in water, dissolves readily in carbonic acid forming the bicarbonate:



The bicarbonate is carried away in solution by the underground waters leaving large caverns. If the crust above

falls into the cavern, it forms what is called a *limestone sink*. The above reaction is reversible. As the water solution of calcium bicarbonate drops from the roof of the cave, some evaporation occurs and carbon dioxid is liberated. Thus the insoluble calcium carbonate which is thrown out of solution hangs from the roof in icicle-like masses called *stalactites*. Upon the floor



(Salisbury's Physiography, by permission.)

FIG. 169.—Stalactites and stalagmites in Marengo cave.

of the cave further precipitation occurs forming *stalagmites*. See Fig. 169.

398. Calcium Oxid. CaO . Calcium oxid, or *quicklime*, is made by heating limestone in large furnaces called *lime-kilns*. In the *continuous action vertical kiln* the limestone is fed into the top of the furnace. The fuel is burned on hearths outside the kiln and the flames and hot gases are drawn up through the limestone on the inside. See Fig. 170. The lime, which is removed at the bottom of the furnace is not contaminated with the ashes from the fuel in this *long flame process*. In the *short flame process* the fuel is mixed with the limestone and the lime is not so pure.



A modern *rotary kiln* is shown in Fig. 171. Limestone or marble scraps are crushed to pieces no larger than walnuts and fed into the upper end of a slowly rotating cylinder which may be 8 ft. in diameter and 125 ft. long. As these lumps work their way along the kiln they meet the hot gases from the burning fuel, usually oil or gas, and lose all their carbon dioxid by the time they reach the lower end of the kiln. Then the lime drops into another rotating cylinder in which it is cooled. Some of the lime is packed into barrels as *quicklime*, but in many modern plants it is *hydrated* and bagged.

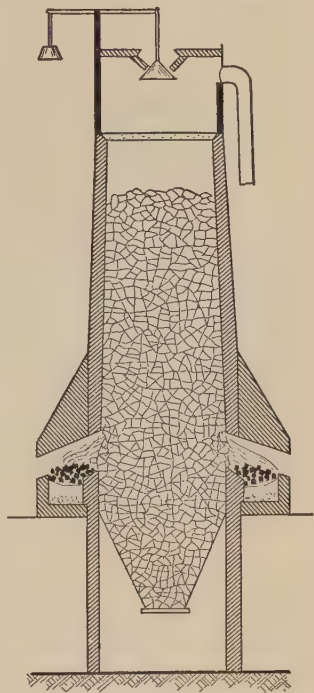


FIG. 170.—Sectional view of a vertical lime-kiln.

399. Properties of Calcium Oxid. Pure calcium oxid is a soft, white, amorphous compound. It is very refractory,

melting or vaporizing only at the temperature of the electric arc. It unites chemically with water to form calcium hydroxid or *hydrated lime*.



As the lime unites with the water it swells up, and large quantities of heat are evolved. Wooden containers of lime often burst and may be set on fire by the heat produced if the product in them gets wet. Quicklime gradually takes moisture from the air forming first the hydroxid and then taking

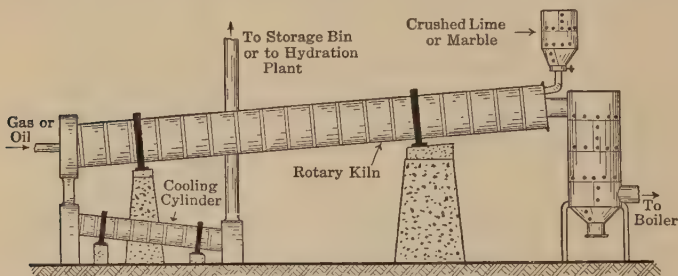


FIG. 171.—Rotary kiln for making lime.

on carbon dioxid to form the carbonate. Such *air-slaked lime* is a mixture of calcium hydroxid and calcium carbonate. It is not suitable for use in making mortar or plaster.

400. Calcium Hydroxid. Ca(OH)_2 . Calcium hydroxid, which we have seen is made by *slaking* calcium oxid, is a white solid, only slightly soluble in water. Its water solution, known as *limewater*, is a strong base. Since calcium hydroxid is the cheapest base, it finds extensive application, being used to remove hair from hides, in *liming* soils, in the manufacture of ammonia, glass, and bleaching powder, and in softening hard water. A suspension of calcium hydroxid in water, called *milk of lime*, is used for whitewash.

To prevent the dangers from fire and to decrease air-slaking during transportation much quicklime is now *hy-*

drated at the kiln. The quicklime is stirred mechanically with just enough water to combine with the weight of lime present.

One of the most important uses of slaked lime is in the preparation of mortar. *Lime mortar* consists of a mixture of freshly slaked lime and sand. To make a harder mortar and one that will resist weathering to a greater degree, cement is

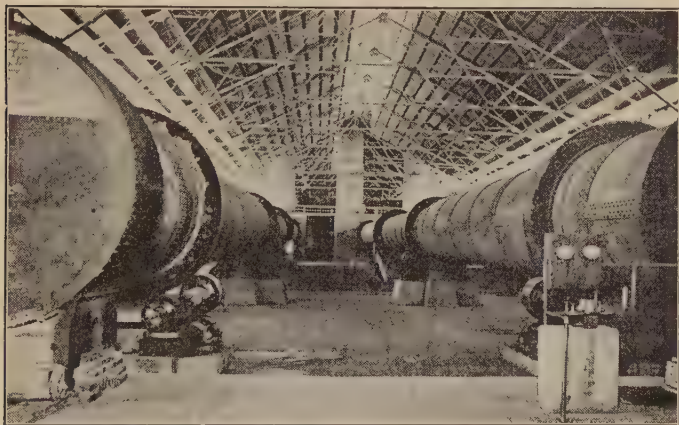
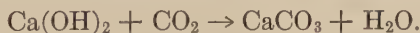


FIG. 172.—Rotary cement kilns.

often used instead of part or all of the lime in making mortar. During the hardening or “setting” of mortar, water is first lost by evaporation. Then carbon dioxid is *slowly* taken up from the air, especially at the surface, resulting in the formation of calcium carbonate while water is liberated:



Thus the calcium hydroxid gradually changes into a hard stony mass. It probably requires years before all the hydroxid is changed into the carbonate. The sand makes the mortar porous, thus giving a more free circulation of air. It also prevents undue contraction or shrinkage and increases

the hardness and strength of the mass. When mortar is to be used for plastering, hair is generally added to make it cling together better until hardening occurs.

401. Cement. Some limestone rocks contain a certain percentage of clay. When they are heated and pulverized they form what is called a *hydraulic cement*. Such a cement hardens even under water. Rocks that form cement in this manner are known as *natural cements*.

Portland or artificial cement is made by heating an artificial mixture of limestone and clay and then grinding the

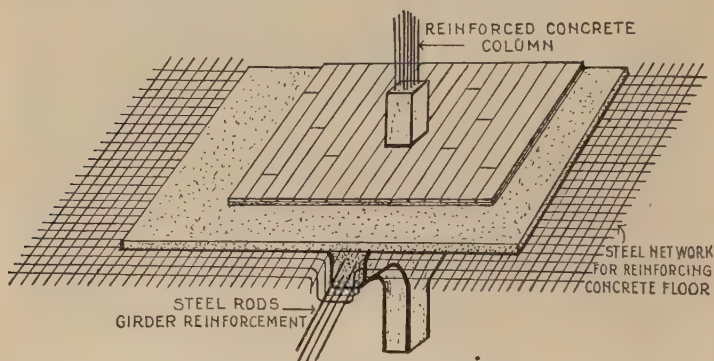


FIG. 173.—Methods of reinforcing concrete.

product to a very fine powder. Such a mixture is ground and then heated in a rotary kiln very similar in construction to a rotary limekiln. See Fig. 172. Powdered coal, oil, or gas may be used as a fuel. By the time the mixture reaches the lower end of the kiln it has been heated until it just begins to melt. Thus it leaves the kiln as a clinker which is then ground to a powder so fine that 92% should pass through a 100-mesh sieve. To prevent too rapid "setting," 2 or 3% of gypsum is usually ground with the clinker.

The hardening of cement is not well understood; it appears to be partially due to the union of its components with water

to form hydrates. Some believe the action is colloidal, since it is possible to make a gel by agitating very fine cement with water.

Concrete is made by mixing together cement, water, sand, and crushed stone or cinders. Upon "setting" it forms a very hard compact mass. Thus it is used for making building blocks, sidewalks, streets and roads, bridges, foundations, floors, the walls of dams, and for numerous other purposes.



FIG. 174.—Steel wire in position for reinforcing concrete.

Reinforced concrete is concrete that is strengthened by embedding in it rods of iron or steel. See Fig. 173. It is used extensively in structural work. See Figs. 174 and 175. Concrete is sometimes applied by means of an atomizer or cement gun. See Fig. 176. The United States produces about 100,000,000 barrels of cement annually. As timber becomes scarce and the prices continue to rise, the applications of cement become more varied and the quantity used continues to increase. See Fig. 177. Pebbles and cement mortar are used in making *stucco* for covering buildings.

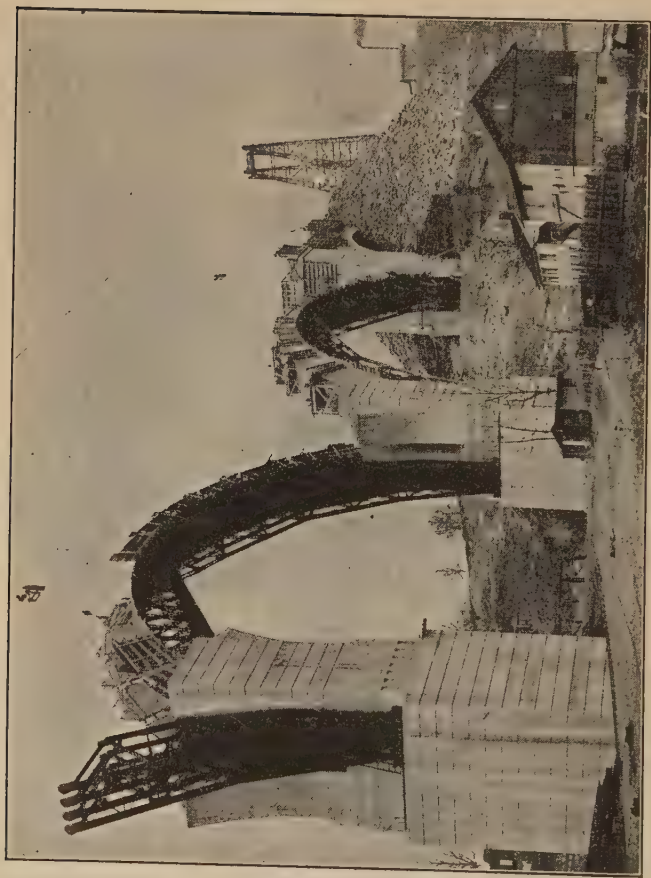


FIG. 175.—Reinforced concrete viaduct.

402. Calcium Sulfate. CaSO_4 . Calcium sulfate occurs in nature as the mineral *gypsum*. Transparent crystals of gypsum are known as selenite. A white opaque variety, known as *alabaster*, is used for statuary. Since it is soft



(Permission of Scientific American.)

FIG. 176.—Concrete atomizer in operation.

enough to be easily scratched with the thumbnail, it is one of the easiest minerals to carve.

When gypsum is heated to a temperature of 110° to 130° C., it loses part of its water of crystallization and forms a white substance known as *plaster of Paris*. When this plaster is mixed with water it sets rapidly, taking on water and forming crystals. It thus hardens to a white substance that finds use in making casts, in plastering when a very white coating is desirable, and in



(Permission of Scientific American.)

FIG. 177.—Relative increase in the amount of cement used from 1880 to 1910, and the corresponding decrease in price.

making one type of stucco, which also contains glue and stone.

The mineral gypsum finds use as a fertilizer under the name of *land plaster*. It is used for calcimining, and as a filler for paper and paints.

403. Bleaching Powder. CaOCl_2 . This compound is made by passing chlorin over thin layers of freshly prepared calcium hydroxid. The chlorin enters the top of the chamber, Fig. 178, where it is absorbed by the calcium hydroxid. Any unabsorbed chlorin passes on to the next chamber. The chamber is aired, and the bleaching powder is packed into metal cans or drums. The product is not very stable and gas is slowly evolved. Enough gas may accumulate to expel some of the grayish white powder forcibly when a can is opened. Care should be used to protect the eyes when opening cans of "chlorid of lime" that have stood for some time. The moisture and carbon dioxid from the air act upon bleaching powder with the evolution of *hypochlorous acid*, HClO . Hence it is a good disinfectant. Large quantities are used for purifying water supplies, as a disinfectant, and in the bleaching industry.

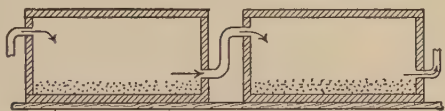


FIG. 178.—Chambers for making bleaching powder.

404. Other Calcium Compounds. Several calcium compounds have already been studied. *Calcium phosphate*, $\text{Ca}_3(\text{PO}_4)_2$, used for making fertilizer; *calcium carbid*, CaC_2 , a product of the electric furnace, used for making acetylene; *calcium cyanamid*, CaCN_2 , used as a fertilizer and for making ammonia; and *calcium chlorid*, CaCl_2 , used as a dehydrating agent. *Calcium bi-sulfite*, $\text{Ca}(\text{HSO}_3)_2$, is a compound which finds extensive use in the making of print paper.

B. BARIUM AND STRONTIUM

405. Barium and strontium are found in nature as sulfates and as carbonates. *Barium sulfate*, BaSO_4 , is a white heavy solid that finds use in a variety of industries. It is used as a filler in making heavy paper, and also in paints. Formerly it

was considered an adulterant in paints, but it has been shown that it increases the durability and wearing qualities of paints. Considerable quantities of barium sulfate are being used in making *lithopone*, a white pigment. *Barium peroxid*, BaO_2 , is a vigorous oxidizing agent; it is used in making hydrogen peroxid. Barium nitrate, $\text{Ba}(\text{NO}_3)_2$, is a white crystalline solid. Since barium compounds impart a yellowish-green color to the flame, they find considerable use in making flares and other fireworks. The nitrate is generally used.

Strontium imparts a bright red color to the flame. Therefore its compounds are used as red fire in pyrotechnical displays. *Strontium nitrate*, $\text{Sr}(\text{NO}_3)_2$, mixed with powdered shellac and lycopodium powder makes a beautiful red light for tableaux.

SUMMARY

The *carbonates* and *sulfates* of calcium, barium, and strontium are important compounds found in nature.

Calcium carbonate is used as limestone for building purposes, as a flux, in making glass, and in the manufacture of quicklime.

Quicklime, or *calcium oxid*, is a white, soft solid that unites with water to form the base *calcium hydroxid*.

When a cheap base is needed for industrial operations, calcium hydroxid is generally used. For softening water, for removing the hair from hides, for making ammonia and bleaching powder, and in the preparation of mortar, calcium hydroxid is used extensively.

Mortar is a mixture of slaked lime, sand, and water. Cement is often used to take the place of part or all of the lime in making mortar. Plaster usually contains the foregoing constituents and hair.

Cement is prepared by heating a mixture of *calcium carbonate* and *clay* and then reducing the product to a very fine powder. With sand, crushed stone, and water, it forms *concrete*, a substance largely used for building materials. Concrete may be reinforced by having embedded in it bars of iron or steel.

Calcium sulfate is used as a fertilizer and in the manufacture of plaster of Paris.

Barium and *strontium* compounds are used in the manufacture of fireworks.

QUESTIONS

1. Why do the walls of freshly plastered houses remain damp for some time?
2. Would limestone be completely converted into lime by heating it in a closed tube? Explain.
3. Why is air-slaked lime not desirable for making mortar?
4. What action occurs when marble is strongly heated? Write the equation.
5. Does marble make good lime? Is it ever used for this purpose?
6. Why does a wood fire aid the hardening of the plaster in a new house?
7. Why does blowing air or steam into a limekiln hasten the production of lime?
8. Compare the "setting" of mortar, plaster of Paris, and cement.
9. Could barium hydroxid be substituted for calcium hydroxid as a base?
10. How can the flame test be used to identify sodium, potassium, barium, and strontium?
11. What is meant by air-slaked lime? Write the equations to show how it is formed from quicklime.
12. Why should care be taken to protect the eyes when opening cans of "chlorid of lime"?

PROBLEMS

1. How many pounds of calcium oxid can be obtained from one ton of limestone, 95% pure? How many pounds of slaked lime will it make?
2. Starting with calcium carbonate, write all the equations for the preparation of calcium oxid, calcium hydroxid, and calcium chlorid. If you started with 250 gm. of pure calcium carbonate, how many cubic centimeters of hydrochloric acid containing 38% HCl would be needed to convert the carbonate into the chlorid. One cubic centimeter of hydrochloric acid weighs 1.2 gm.

CHAPTER XXXIV

THE MAGNESIUM FAMILY

406. The Family. The magnesium family consists of four elements: *magnesium*, *zinc*, *cadmium*, and *mercury*. The resemblance that is so marked in the families just studied is not so close in this group of elements. For example, magnesium is like calcium in some respects and in others it resembles zinc. Mercury is like copper in many of its chemical properties. The properties of this family vary from magnesium, which is quite an active metal, to mercury, which is inactive. The valence of all the members in this family is two, although mercury sometimes has a valence of one.

A. MAGNESIUM

407. Occurrence and Extraction. Magnesium sulfate occurs in some of our Western States and in British Columbia. *Carnallite*, a hydrated double salt of potassium and magnesium chlorids, is found at Stassfurt.

Carnallite forms the chief ore of magnesium. It is heated to drive off the water of crystallization and the magnesium is then obtained by the electrolysis of the fused ore. The ore is melted in an iron container which serves as the cathode. A graphite or carbon rod serves as the anode.

408. Properties and Uses. Magnesium is a silver-white metal having a density of only 1.75. It is ductile when heated, therefore it can be drawn into wire or ribbon. It is not acted upon by dry air but in moist air a coating of basic carbonate forms on its surface. This coat does not scale off and it protects the metal underneath from further tarnishing.

A metal that forms a non-porous, non-scaling coat is said to be "self-protective." In air magnesium burns readily forming the *oxid* mixed with some *nitrid*, Mg_3N_2 . It is one of a few metals that combines directly with nitrogen. The white light that it produces when it burns is very rich in *actinic rays*. Such rays are active in producing chemical action. Magnesium decomposes hot water slowly with the liberation of hydrogen. All common acids attack the metal vigorously.

Mixed with an oxidizing agent, powdered magnesium is used in flashlight powders, flares, star-shells, and in fire-works. It forms an alloy with aluminum that is very light and strong. This alloy, known as *magnalium*, finds use in air-plane and automobile parts, and for the beams of chemical balances.

409. Magnesium Compounds. *Magnesium oxid*, MgO , is a very refractory compound used for lining crucibles, furnaces, and for making fire brick. It is made by heating magnesium carbonate, MgCO_3 , a compound found extensively in nature. It unites with water to form *magnesium hydroxid*, $\text{Mg}(\text{OH})_2$. A suspension of the oxid and hydroxid of magnesium in water is sold as "milk of magnesia." With asbestos or wood fiber, and magnesium chlorid, the oxid of magnesium forms a compound that is used for artificial stone floors.

A basic carbonate of magnesium, so light and fluffy that it is about 90% pores, has been prepared for covering steam-pipes. It is known as "85 per cent magnesia." It is an excellent heat insulator.

Magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, is used in medicine under the name Epsom salts. It finds some use in the dye industry. The silicates of magnesium include such well-known compounds as *talc*, or *soapstone*, *asbestos*, and *meerschauum*. Soapstone is used for table-tops and sinks. When powdered it is known as *talcum powder* or *French chalk*. Asbestos is a fibrous mineral that is manufactured into a

fireproof paper or cloth. Meerschaum is used for pipe-bowls, cigar-holders, etc.

B. ZINC

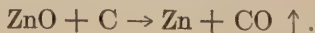
410. Occurrence. Zinc ores occur abundantly in the United States, especially in Missouri, Kansas, Illinois, and New Jersey. A sulfid of zinc, known as *sphalerite* or zinc blend, is a very important ore of zinc, but the metal is also



FIG. 179.—Retorts used in extracting zinc.

extracted from a carbonate known as *smithsonite* and from certain silicates of zinc. *Franklinite*, an oxid of zinc that is mixed with the oxids of iron and manganese, is found in New Jersey.

411. Metallurgy. The method of extracting zinc is very simple. The ore is converted into the oxid, mixed with powdered coal, and heated in earthenware retorts. See Fig. 179. The zinc vaporizes and is condensed in iron or earthenware receivers. The following reaction occurs:



Since the boiling point of zinc is low it may be purified by distillation. Sometimes it is purified by electrolysis.

412. Properties. Zinc is a bluish-white metal. At the ordinary temperature it is somewhat brittle but at a slightly increased temperature it becomes malleable and ductile. Rolled or drawn zinc does not become brittle when it is subsequently cooled. Zinc burns in the air with a bluish-white flame forming zinc oxid. Dry air does not affect zinc, but moist air attacks it forming a basic carbonate.



FIG. 180.—The workman at the left shoves the article to be galvanized into the left portion of the vat and it is removed by the other man. The molten zinc in the left compartment is covered with a layer of sawdust and ammonium chlorid.

The tarnish thus formed is adherent. Therefore zinc is a self-protective metal. All the ordinary acids act upon zinc which contains a trace of impurity. Chemically pure zinc is acted upon very slowly by acids. The active bases, sodium and potassium hydroxids, dissolve zinc with the evolution of hydrogen. Soluble zincates are formed.



413. Uses of Zinc. Large quantities of zinc are used for making *galvanized iron*. The iron is thoroughly cleaned by "pickling" and then dipped into molten zinc. The zinc that adheres to the iron is beautifully crystalline. It prevents the rusting of iron. See Fig. 180. In some cases galvanizing is done by plating the iron with zinc, and in a method known as *sherardizing*, the zinc is vaporized and

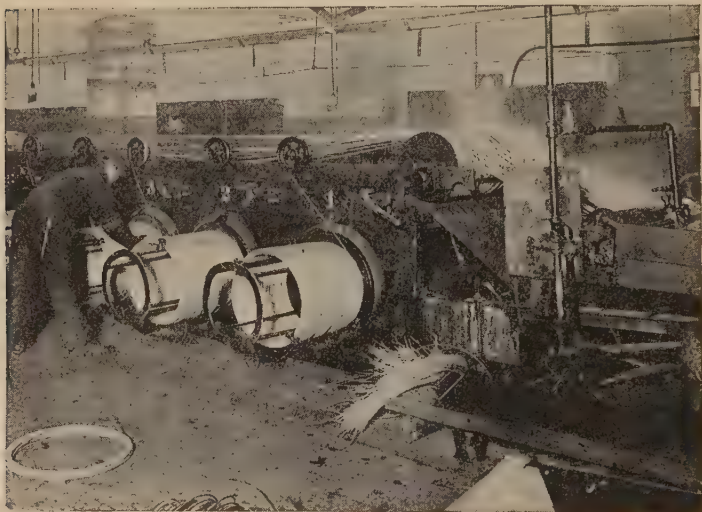


FIG. 181.—Iron wire is unrolled, passed through a vat of molten zinc, and then re-rolled after the galvanizing process.

then condensed on the object to be plated. Wire is galvanized by pulling it through a bath of melted zinc. See Fig. 181. Occupying the position it does in the electromotive series, zinc is a suitable element for use as the negative element in voltaic cells. Practically all types of voltaic cells use zinc as the negative plate.

Zinc forms some very useful alloys. *Brass* is an alloy of zinc and copper. *Bronze* contains copper and tin; zinc is

sometimes added. *German silver*, now commonly called *nickel silver*, is an alloy containing copper, nickel, and zinc. It is a bronze in which nickel replaces tin.

414. Compounds of Zinc. *Zinc oxid*, ZnO , is one of the most important compounds of zinc. It is a white solid that finds use as a paint base under the name *zinc white*. It is much whiter than white lead, and while its covering power is not so great, it does not darken when exposed to gas fumes or air containing hydrogen sulfid. Used alone as a paint, it peels badly, but it is very satisfactory when mixed with lead or some other paint base. Considerable quantities of zinc oxid are used as a filler for rubber in the tire industry. *Zinc ointment* contains zinc oxid or zinc stearate in a base of some kind of grease.

Zinc chlorid, ZnCl_2 , is a white, deliquescent solid. It finds some use in preserving wood that is to be used in contact with the earth, such as railroad ties, posts, etc., although creosote is now more widely used for this purpose. Zinc chlorid is used as a soldering fluid. Zinc chlorid attacks wood fiber and forms a *cellulose hydrate*. This makes it suitable for use in making fiber board, or "vulcanized fiber," a strong, tough product employed in making boxes, trunks, washers, and insulating material.

Zinc sulfid, ZnS , is used with barium sulfate as a white pigment, known as lithopone. *Zinc sulfate*, ZnSO_4 , is a white, crystalline solid used in the manufacture of lithopone. It also finds use in making cotton print goods, as a disinfectant, and in medicine as an emetic. *All soluble salts of zinc are poisonous.*

C. CADMIUM

415. Cadmium is usually found in nature associated with zinc. It resembles magnesium and zinc in its properties. Cadmium is used in some of the fusible alloys. *Cadmium sulfid*, CdS , is a yellow compound used as an artist's color.

D. MERCURY

416. Occurrence. Small quantities of mercury are found uncombined, but the chief ore is mercuric sulfid, a red mineral known as *cinnabar*. Mercury is commonly called quicksilver. The mercury mines of Spain are the richest in the world. Mercury is also found in California and Austria. Mercury is extracted by roasting the ore. The metal is purified by distillation.

417. Properties. Mercury is a heavy, silver-white metal with a metallic luster. It is the only metal that is liquid at the ordinary temperature. Mercury freezes at about -39° C. and boils at 357° C. It is 13.6 times as dense as water. Such common metals as iron, zinc, copper, tin, and lead float on mercury.

Mercury does not tarnish when exposed to the air. When heated in the air it slowly changes into a red powder, *mercuric oxid*, HgO . Since mercury stands below hydrogen in the replacement series, it can not replace that element from hydrochloric acid. Such strong acids as nitric and sulfuric act upon it, nitric acid very vigorously. Hydrogen is not liberated in such cases, but it unites with a part of the oxygen of the acid to form water, and such reduction compounds as nitric oxid, nitrogen peroxid, or sulfur dioxid are set free respectively.

418. Uses. The following properties of mercury make it suitable for use in thermometers: (1) It has quite a low freezing point and a high boiling point; (2) it has a much higher coefficient of expansion than glass; (3) its expansion is quite uniform, especially between 0° C. and 100° C. To illustrate, a column of mercury increases the same amount when heated from 20° to 21° C. that it does when heated from 40° to 41° C. Mercury is suitable for use in barometers since it has so high a specific weight. Mercury is a fairly good conductor of electricity; it is convenient for such use when

a good contact is desired. Mercury finds some use in the collection of soluble gases and in certain kinds of air-pumps. Mercury is also used in the Cooper-Hewitt mercury vapor arc lamps and in arc rectifiers, and in the manufacture of fulminating mercury.

Mercury forms alloys with many other metals known as *amalgams*. In extracting gold and silver the powdered mineral containing these precious metals is treated with mercury to form amalgams from which the gold and silver may be recovered by distilling the mercury. *Tin amalgam* is used for the backs of cheap mirrors. An amalgam consisting largely of silver, tin, and mercury is used for filling teeth. The zincs used in voltaic cells are amalgamated with mercury to prevent local action between zinc and its impurities. Amalgams appear to be solutions of metals in mercury, or in some cases definite compounds.

419. Compounds of Mercury. Mercury forms two classes of compounds: *mercurous*, in which the valence of the element is one; and *mercuric*, in which the valence is two. The chlorids of mercury are the most useful compounds of this element.

Mercurous chlorid, Hg_2Cl_2 , is a white solid, quite insoluble in water. It is used in medicine as a liver stimulant under the name of *calomel*. When exposed to the light, this chlorid forms mercuric chlorid and metallic mercury. Calomel tablets that have been darkened by exposure to light should never be taken, *since mercuric chlorid is extremely poisonous*.

Mercuric chlorid, HgCl_2 , forms beautiful white crystals. This chlorid, which is commonly called the *bichlorid of mercury* or *corrosive sublimate*, dissolves quite readily in water. One part of the salt to 1000 parts of water forms a good antiseptic solution, although other less poisonous disinfectants are known. Sometimes it is used medicinally, but the dose is $1/64$ of a grain, and there are 7000 grains in an avoirdupois pound. *Bichlorid of mercury tablets have no*

place in the family medicine cabinet. The whites of raw eggs, or raw milk, may be used as an antidote for mercury poisoning, since the mercury combines with the albumin of the eggs or milk to form an insoluble compound.

Mercuric oxid, HgO , finds some use as red precipitate, and *mercuric sulfid*, HgS , may be sublimed to form a red solid used as a pigment under the name *vermilion*. Mercury pigments have been used on the bottoms of ships to prevent fouling.

SUMMARY

Magnesium is an active silver-white metal. It burns with a very intense white light. It finds use in flashlight powders, fireworks, and in the alloy *magnalium*. The oxid, sulfate, and several natural silicates are the most important compounds of magnesium.

Zinc is bluish-white. It is self-protective, hence it forms a good coating for the protection of iron. It interacts with acids forming salts of which the sulfate and chlorid are the most important. *Zinc oxid* is a very important compound finding use as a paint base. Brass, bronze, and German silver are alloys containing zinc.

Mercury is the only metal that is liquid at the ordinary temperature. It is quite inactive, air or hydrochloric acid having no effect upon it. It dissolves in nitric acid and hot concentrated sulfuric. Mercury finds considerable use in the manufacture of scientific instruments. Its alloys are called *amalgams*.

Mercuric sulfid is a red pigment known as *vermilion*. Two chlorids are important: mercurous chlorid, or *calomel*, is used as medicine; mercuric chlorid, or *corrosive sublimate*, is used as an antiseptic.

QUESTIONS

1. Account for the explosive nature of flashlight powders.
2. Write the equation to show the chemical action that occurs when a strip of zinc is immersed in a solution of copper nitrate. In a solution of mercuric nitrate.
3. Name two important alloys of zinc, of bismuth, and of antimony. Of what is each composed?
4. Hydrogen sulfid turns white lead black. Why does it not discolor zinc white?
5. What is meant by a refractory? Give two or three examples.

6. Why should active poisons never be kept in the medicine cabinet? What do you think of the suggestion that dangerous poisons be dispensed in irregularly-shaped bottles?

7. Would you expect a solution of zinc chlorid to react acid or alkaline? Why is this solution used in soldering?

8. Name three methods used to prevent the decay of wood.

9. What properties has mercury that make it suitable for use in thermometers? In barometers?

10. What compound do you think would be formed by heating a mixture of mercuric chlorid and mercury?

11. What is meant by a heat insulator? Name as many places about the house as you can where heat insulators are desirable.

12. How would you treat a case of poisoning by a salt of mercury?

CHAPTER XXXV

THE ALUMINUM FAMILY

420. Introductory. Of the several elements in this group, *boron* and *aluminum* are the only ones of sufficient importance to merit discussion in an elementary text. The similarity between boron and aluminum is not well-marked. Boron is really an acid-forming element that resembles silicon somewhat in its chemical properties. Aluminum is a base former, but its hydroxid is *amphoteric*. Elements in this group have a valence of three.

A. BORON

421. Boron. In the alkaline desert regions of Southern California and Nevada extensive beds of *borax*, or sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and *colemanite*, or calcium borate, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, are found. These beds supply the boron for making boric acid and for the borax industry.

The element *boron* has been isolated, but it has no practical value. Two of its compounds are important substances, boric acid and borax. *Boric acid*, H_3BO_3 , crystallizes in white, lustrous scales. It occurs in nature in volcanic regions, especially in Tuscany, where it issues from the earth in steam-jets. Boric acid is a weak acid; its vapor imparts a green color to the flame. It has antiseptic properties, and is used as an eye-wash and mouth-wash. It has been used as a preservative. Some doctors believe that boric acid will cause indigestion, if it is used continuously for sterilizing milk-bottles for babies.

Borax find use as a mordant, an antiseptic and preservative, and in small quantities for softening hard water.

Since it dissolves metallic oxids, it is used as a flux in soldering and welding to give a clean surface. Borax fuses to a clear, colorless bead which is colored by traces of various metals. Thus the borax bead is used in the laboratory to test for such metals as cobalt, nickel, manganese, and iron. The borates of certain metals are quite extensively used for

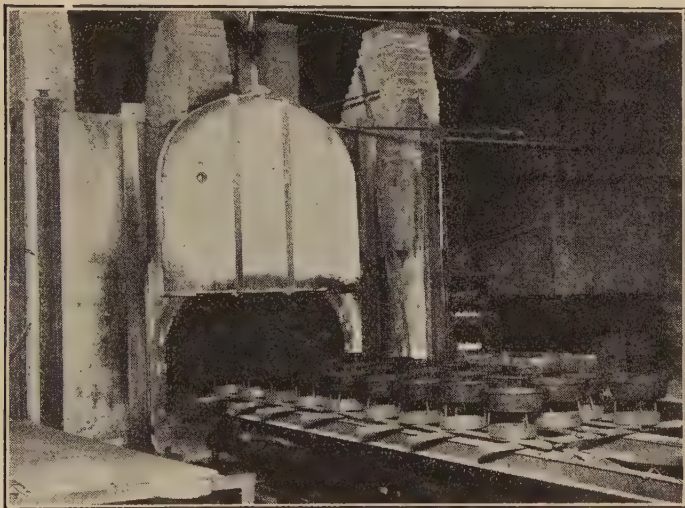


FIG. 182.—The mixture for enameling is fused, poured into cold water, and then powdered. The iron pan is dipped into a suspension of this powder in water and then heated in a furnace long enough to fuse the coating.

making glazes and enamels. We have learned that some glass contains borosilicates. Fig. 182 shows some enamel ware that has just been removed from the furnace.

B. ALUMINUM

422. Properties. Aluminum is a white metal whose specific weight is only 2.6; it is only one-third as heavy as iron. It is both malleable and ductile, but not so tenacious

as brass, copper, or steel. Aluminum is a good conductor of heat and electricity, being surpassed in this respect by silver, copper, and gold only. It may be welded or cast, but it can be soldered only with difficulty.

Although aluminum takes a high polish, it soon becomes dull as a result of the formation of a very thin coating of the oxid. This gives the metal a slight bluish tint. It is a self-protective metal. Hydrochloric acid acts readily on aluminum. Nitric acid hardly affects it at all. Hot, concentrated sulfuric acid dissolves aluminum forming the sulfate. Salt water corrodes aluminum rapidly and the alkalis interact with it readily.

423. Uses. To some extent aluminum is taking the place of copper as an electrical conductor, since a larger wire may be used with less strain on the support. As a *purifier*, aluminum is used to combine with gases that tend to make steel porous. The use of aluminum in thermit and in the extraction of metals has already been studied. Powdered aluminum is used as a protective paint, as in the "silvering" of radiators. When quite pure, aluminum makes excellent cooking utensils, since it is light, a good conductor of heat, and not easily tarnished. Its salts are not poisonous. For wrapping food and candy aluminum foil is now used extensively to take the place of tin foil.

Aluminum bronze is an alloy of aluminum and copper. It is hard, elastic, of a golden color, and takes a high polish. When a smaller percentage of copper is used, aluminum bronze resembles silver. *Magnalium* is an alloy of aluminum and magnesium. *Duralumin* is an alloy of aluminum, copper, and manganese that is less than half as dense as steel and nearly as strong. The framework of the Shenandoah is made of this alloy.

424. Aluminum Oxid. Al_2O_3 . Corundum and emery are natural oxids of aluminum. Rubies and sapphires are pure specimens of aluminum oxid colored by the presence

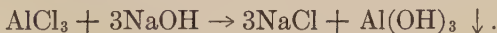
of traces of metallic oxids. Synthetic rubies and sapphires are now made from molten aluminum oxid. The white sapphire consists of the pure oxid. Blue sapphires are colored by titanium oxid, rubies by chromium. These artificial gems are identical in color and properties with the natural stones and can not be distinguished from them. *Emery* is used as an abrasive in the form of emery paper, cloth, or as grinding wheels. *Alundum* is an artificial oxid



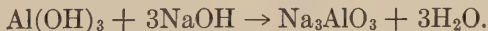
FIG. 183.—Alundum, a much used abrasive.

of aluminum made by fusing bauxite in an electric furnace. It is used for making crucibles for laboratory use and as an abrasive. See Fig. 183.

425. Aluminum Hydroxid. $\text{Al}(\text{OH})_3$. When sodium hydroxid is added to a solution of an aluminum salt, a white, gelatinous precipitate of aluminum hydroxid is formed:



This precipitate is insoluble in water but it dissolves, forming sodium aluminate, if we add the sodium hydroxid in excess.



This reaction shows the amphoteric nature of aluminum hydroxid. In the presence of a strong acid it ionizes to form a very feeble base:



When treated with a strong base like sodium or potassium hydroxid it ionizes as a very weak acid:



Aluminum hydroxid is such a weak base that its salts with weak acids are almost completely hydrolyzed. We would *expect* to have aluminum carbonate precipitated if we add sodium carbonate to a solution of aluminum chlorid:



Such is not the case.

If any aluminum carbonate is formed it instantly hydrolyzes to form the hydroxid:



Aluminum hydroxid is also precipitated when sodium *sulfid* is added to the solution of an aluminum salt.

Aluminum hydroxid is used in the coagulum method of purifying water and as a *mordant* in dyeing cotton and linen fabrics. Aluminum hydroxid unites with many dyes to form an insoluble compound known as a *lake*. Many dyes do not adhere directly to cotton and linen but such a gelatinous substance as aluminum hydroxid readily sticks to the fibers. When the fibers have been impregnated with such a compound, usually by hydrolysis, and then dipped in the dye bath, the dye unites with the mordant to precipitate a lake on the fibers. Thus the mordant *fixes* the dye so it does not wash out. Lakes of different colors may be pro-

duced with the same dye by varying the mordant. Lakes are often used as pigments.

426. Dyeing. Formerly the chief source of dyes was from animal, plant, and mineral compounds. In 1856 Perkin succeeded in preparing mauve artificially from a coal tar product by oxidizing aniline. Now a great many dyes are made synthetically from coal tar, a substance that before the above date was considered almost worthless.

A good dye should have a pleasing shade; it should not fade when exposed to the light; it should not be removed from the fabric by rubbing, washing, or perspiration; it should not weaken the fiber. Wool and silk are sometimes dyed directly, as these fibers combine with certain dyes without the use of a mordant.

Some *insoluble* dyes such as indigo are precipitated on the fiber. Indigo is now prepared artificially. In the presence of a reducing agent it forms indigo white, a compound soluble in alkalis. When textile fibers are saturated with a solution of indigo white and then exposed to the air, oxidation occurs, resulting in the formation of the insoluble indigo blue. This dye is extensively used in dyeing blue serge. The color is very fast.

Acid dyes, which consist of alkali or calcium salts of color acids, are used in acid solution. They are not used for dyeing cotton and linen, but they dye silk and wool directly. Acid dyes are very fast to light, but they can not be washed with a soap or powder containing any free alkali, since a base causes the acid dye to dissolve rapidly.

On the other hand, *basic dyes* fade quite rapidly when exposed to the light, but they are not removed by washing. They dye wool and silk directly, but when used with cotton or linen, a mordant is required. Such dyes as methyl violet, methylene blue, malachite green, fuchsine, etc., are examples of basic dyes.

To secure good results in dyeing, the fabric must be

thoroughly cleansed; it should be wet when introduced into the dye bath; the dye should be kept slowly boiling; and the goods should be agitated so all parts will be dyed uniformly. In dyeing cotton goods, the addition of such salts as sodium chlorid or sodium sulfate makes the dye less soluble and causes more of it to unite with the fabric.

In 1914 when the World War started there were only six or seven concerns in the United States making any dyes at all. Nearly all the colors used here were being imported from Germany. Dyes became scarce and many of them were unsatisfactory, in many cases because a dye intended for one purpose had to be used for another. Then some jobbers who had stocks of dyes on hand diluted them with salts to the extent of 99% in certain cases. The chemists in America attacked with great vigor the problem of building up a dye industry, and at the present time about 90% of the dyes used here are made in America.

427. Alums. If we mix solutions of potassium sulfate and aluminum sulfate and then evaporate the mixture, a *double salt* separates as crystals. The formula of this alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. Any double sulfate formed in the same manner and having similar properties is called an *alum*. Instead of potassium sulfate, either sodium or ammonium sulfate is often used. Such trivalent metals as iron and chromium may take the place of the aluminum. The general formula, $M'_2 M'''_2 (SO_4)_4 \cdot 24H_2O$, is used to represent alums, in which M' is some univalent element, or group, and M''' a trivalent metal. Alums are used as mordants. *Aluminum sulfate*, $Al_2(SO_4)_3$, is used largely instead of alum for water purification and as a mordant.

428. Silicates of Aluminum. *Fuller's earth* is a silicate of aluminum used for cleaning fabrics and for clarifying oils. *Ordinary mica* is a potassium aluminum silicate. It is translucent and infusible. Under the *incorrect* name of isinglass it is used in stoves. As an insulator mica is used



(Copyright by Keystone View Company.)

FIG. 184.—Kilns in which the famous Satsuma pottery is fired.

in making commutators for dynamos and motors. The *feldspars* are complex silicates, usually containing aluminum silicate with either sodium or potassium silicate. By the action of water and carbon dioxide, disintegration or weathering occurs and the alkalis are leached out as soluble silicates or carbonates leaving a *white clay*, or hydrated aluminum silicate, known as *kaolin*. The colored clays found in soils usually contain iron and sometimes calcium, the color being largely due to iron compounds. *Ultramarine* is a complex substance made by heating together clay, soda, and sulfur. It is found in nature as the mineral *lapis lazuli*. The artificial product is a more highly colored pigment; it is used also as a laundry blue, and to neutralize the yellow tint of sugar, wood pulp, and linen fibers.

429. Applications of Clays. Clay becomes plastic when it is mixed with water and it can be molded into any desired shape. When the plastic mass is dried and baked at a high temperature it does not melt but it contracts and forms a hard porous mass capable of resisting pressure. This property of clay makes it suitable for use in making *brick, earthenware, and porcelain*. In making bricks an impure clay is used. The red color is due to the presence of iron compounds. In making *vitrified brick* a high enough temperature is used to start fusion, thus filling the pores at the surface. *Fire bricks* are made of clay and sand. *Earthenware* and *tile* are made from coarse clays and a low temperature is used in "firing," so the mass remains porous. Flower pots are examples of this ware. When such clays are heated to a higher temperature they are vitrified throughout the mass forming *stoneware*. The cheaper kinds of stoneware are glazed by throwing salt into the furnace. *Porcelain or china* is made from a very pure white clay mixed with powdered feldspar. It is usually fired twice. After the first firing the porous biscuit is dipped into water containing in suspension a mixture of powdered feldspar

and kaolin. During the second firing the feldspar melts and fills the pores so that the china becomes impervious to liquids. See Fig. 184.

SUMMARY

Boric acid and *borax* are the most important compounds of boron. Both find some use as antiseptics and preservatives. Borax is used in soldering and welding to dissolve the tarnish and give a clean surface.

Aluminum is a light, white metal. It is a good conductor of heat and electricity. It is self-protective. Aluminum is used for paint, to purify steel, for electrical conductors, and in making cooking utensils.

Natural and synthetic rubies and sapphires consist of *aluminum oxid*. Impure aluminum oxid is used as an abrasive.

Aluminum hydroxid may act as a base or an acid. It is used in purifying water and as a mordant.

Alums are *double sulfates* that find some use as mordants.

Mica, clay, and fuller's earth are silicates of aluminum. Clay is used in making bricks, earthenware, stoneware, and porcelain.

QUESTIONS

1. What precautions should be taken in using aluminum cooking utensils?

2. What advantages has aluminum when used for cooking utensils?

3. What are the purposes of a mordant? What is a lake?

4. What elements have we studied that act as either acid formers or base formers? In what groups in the periodic table are these elements found?

5. Why is aluminum hydroxid precipitated when a solution of sodium carbonate is added to the solution of an aluminum salt?

6. Write the equations to show what action occurs when sodium sulfid is added to a solution of aluminum chlorid.

7. Aluminum acetate is the aluminum salt of a weak acid. What reaction do you think would occur if a piece of cloth were soaked in aluminum acetate and then treated with steam?

8. Why should alkaline scouring powders not be used for washing aluminum ware?
9. Should aluminum ware be polished frequently? Give a reason for your answer.
10. What is an abrasive? Name several that we have studied.
11. How is aluminum used as a reducing agent?

CHAPTER XXXVI

SOILS AND FERTILIZERS

A. SOILS

430. Bed Rock, the Source of Soils. The bulk of the earth's crust is made up of solid rock, or what is commonly called *bed rock*. When such agents as oxygen, carbon dioxide, water, and other substances, act upon bed rock, they convert it into *mantle rock* or *soil*. The process by which bed rock is converted into mantle rock is known as *weathering*. Plants and animals, wind, and alternate freezing and thawing also aid in breaking large masses of rock up into smaller fragments.

Soils formed by weathering may remain just where they were formed, or they may be transported to another locality. In the first case they form *residual soil*. Wind, running water, and glaciers are the most important agents engaged in transporting soil. Much of the deep, fertile soil of the Middle West was brought down from Canada by prehistoric glaciers. Running water often carries the most fertile part of one farm downstream to some other farm where it is deposited, or it may be carried into the ocean and lost as farm soil. The depth of the soil varies from a few feet in some places to scores of feet in others.

431. Kinds of Soil. The nature of a soil depends upon the constituents of the rock from which it was formed. When sandstone weathers a *sandy* soil is formed; the disintegration of limestone forms a *limy* soil; *clay* soils are formed by the weathering of shale, slate, feldspar, and granite. Granite is a mixed rock; when the quartz it contains weathers sand is the product formed; when the mica and feldspar weather, clay

is produced. A transported soil is quite apt to be a mixed soil since the transporting agent may bring the materials of which it is composed from different sources. A mixture of sand and clay is called *loam*. If the amount of clay is relatively large, it is called a *clay loam*; if it is small in proportion to the amount of sand, the soil is a *sandy loam*. The decomposition of organic matter in the soil forms *humus*. When the decay of organic matter is quite rapid, on account of its being exposed first to the air and then to water, *muck* is formed. It is soft and spongy, and has usually lost all resemblance to the organic matter from which it was formed.

432. Elements Needed by Plants. The elements absolutely needed by plants include *carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, calcium, iron, and magnesium*. *Chlorin, silicon, and sodium* are essential to the *full* development of certain plants. Carbon is obtained from the carbon dioxid of the air; oxygen from the air and soil water; and hydrogen from the soil water that enters the plant through its roots. The other elements must be obtained from the soil. Since the compounds that contain these elements are usually solids, they can not be absorbed by the roots of the plant unless they dissolve readily in the soil water. Recent experiments show that *manganese* produces a decided effect upon the growth of plants. It appears to act as a stimulant in some cases, and in others as a real plant food.

433. Fertility of Soils. A fertile soil contains all the elements essential to a proper development of plants. These elements must be in an *available* form. A poor soil is deficient in one or more important constituents needed for plant growth. A soil may lose its fertility: (1) by the continual removal of the essentials required by plants during successive harvesting of crops; (2) by the leaching out of the soluble matter by water. A loam containing humus is

generally a very fertile soil. The humus increases the capacity of a soil for holding water. It makes a clay soil more easily worked, and it supplies nitrogen for the growth of plants.

A soil may contain all the elements needed for plant growth and yet not be fertile. The *colloidal* nature of a soil affects its fertility, since its ability to adsorb water and mineral salts depends upon the size of the particles present. In many cases the water stands on a piece of ground causing the soil to become *sour* or *acid*. Throughout the Middle West much underground drainage is needed. Porous tile laid beneath the reach of the frost are extensively used in flat sections to carry off the excess water rather rapidly. On the other hand, the rainfall in some regions is so scanty that irrigation must be used to grow crops successfully.

Nearly all soils contain sufficient silicon, iron, magnesium, sodium, chlorine, calcium, and sulfur to supply the needs of plants. For the growth of certain plants that require a large amount of sulfur and calcium, such as onions, garlic, cabbage, etc., the addition of a compound containing these elements is necessary. *Calcium sulfate*, often called land plaster, is the compound generally used. Most soils also contain *nitrogen*, *phosphorus*, and *potassium*, but these elements are taken from the soil more rapidly by plants and they must be replaced to keep the soil fertile. A sandy soil is apt to be deficient in potassium; soluble matter, or available mineral matter, may quite easily be leached out of such a soil. In fact the rain water carries away to the ocean more valuable mineral matter every year from a soil than the plants can possibly remove. In a clay soil, potassium is practically always present, since *clay* is a *potassium aluminum silicate*. Feldspar contains potassium, and granite rocks generally contain considerable calcium phosphate. Thus the weathering of granite and feldspar supplies potassium and possibly phosphorus for plant use. Limestone often

contains fossils that furnish a soil with phosphorus from the bones of animals.

B. FERTILIZERS

434. Fertilizers. Fertilizers are often classed as natural and commercial. Before a farmer can tell just what fertilizers a soil needs, an accurate analysis of the soil must be made by a trained chemist. The farmer can, however, by a systematic application of fertilizers for a period of several years, learn what elements the soil needs most. Soils are classed as alkaline, acid, or neutral, according to their reac-



FIG. 185.—Effect of calcium carbonate in neutralizing the acidity of a muck soil, thus making the nitrogen available.

tion toward litmus. Acid soils are not suitable for the growth of certain plants, especially legumes and certain root-crops. The acidity of a soil may be corrected by the addition of *lime*, *marl*, or *powdered limestone*. Air-slaked lime is better than freshly prepared lime since it is not so caustic and consequently not so likely to injure vegetation. Fig. 185 shows the effect of calcium carbonate upon the growth of cabbage in a very acid muck soil. The letters on the pots show what fertilizers were used with the limestone. The results show the effect of neutralizing the acidity of the soil, thus making the nitrogen available. Care should be taken to avoid excessive use of lime, since it may destroy the humus and cause the soil to lose its fertility.

There is an old proverb that lime makes a rich father but a poor son.

A complete commercial fertilizer contains potassium, nitrogen, and phosphorus. Fig. 186 shows how the analysis of a fertilizer is marked on the bag. The nitrogen may be in any form, but it is generally stated as "equivalent to ammonia." For example, if a manufacturer uses 100 lb. of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, in making a ton of fertilizer, the product contains 5% of ammonium sulfate. But approximately 25% of ammonium sulfate is ammonia, NH_3 , so such a fertilizer contains 25% of 5%, or 1.25% of ammonia or its equivalent. One per cent of sodium nitrate is equivalent to one-fifth of 1% ammonia. Potassium, or potash, is figured as "equivalent to potassium oxid, K_2O ." One per cent of potassium sulfate is equivalent to 0.63 of 1% of K_2O ;

potassium chlorid, KCl , is richer, 1% being equivalent to 0.74 of 1% of K_2O . In the case of phosphorus, the analysis is stated in terms of "total phosphoric acid" and "soluble phosphoric acid." The soluble phosphoric acid is available for immediate use. One per cent of *secondary calcium phosphate* (see section 298) is equivalent to 0.83 of 1% of phosphoric acid.

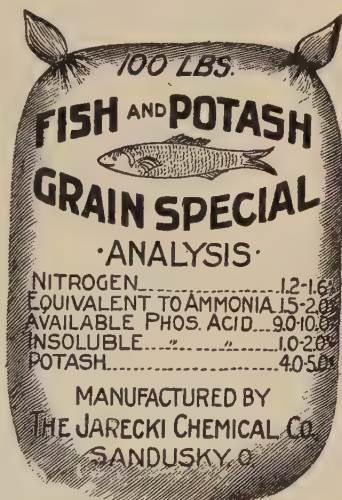


FIG. 186.—A fertilizer bag, showing analysis.

C. NITROGEN FERTILIZERS

435. Nitrogen Fertilizers. Some of the sources of nitrogen were mentioned when we studied the element itself.

Stable manure is rich in nitrogen, as is all decaying animal and vegetable matter. Such products as tankage, fish scrap, slaughter house refuse, dried blood, and guano are also extensively used. The sodium nitrate that is sold for fertilizer is about 16% nitrogen; hence about 6 lb. of the nitrate are needed to furnish 1 lb. of nitrogen. It is very soluble in water so that it may be readily taken up by plants. It



FIG. 187.—Effect of sodium nitrate upon the yield of wheat per acre.

is more apt to be leached from the soils than some of the substances named above. This defect is overcome by using successive applications of the nitrate. Calcium nitrate is also used to some extent as a fertilizer. It contains a slightly higher per cent of nitrogen than the sodium nitrate. Fig. 187 shows the effect of sodium nitrate on the growth of wheat.

Ammonium sulfate is a by-product obtained in making coal gas. It contains more than 21% of nitrogen and it is readily soluble.

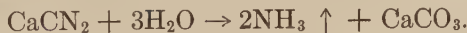
Calcium cyanamid (CaCN_2) is a nitrogen compound that has come into more recent use as a fertilizer. It is not so soluble as either the nitrates or the ammonium sulfate mentioned above, but it has the advantage of being less easily washed out of the soil. In the soil it undergoes chemical changes that convert it into ammonium compounds. In our



(Permission of Scientific American.)

FIG. 188.—Oats grown with and without calcium cyanamid as a fertilizer.

discussion of the plant at Muscle Shoals, we learned that calcium cyanamid decomposes into ammonia and calcium carbonate when treated with superheated steam.



The calcium carbonate which is formed is useful in neutralizing the acidity of the soil. See Fig. 188.

D. PHOSPHORUS FERTILIZERS

436. Phosphorus Fertilizers. Rock phosphates which are found in Florida, Tennessee, and South Carolina, are phosphates of calcium. Some of the Western States also contain deposits of rock phosphate. The origin of such deposits is probably from the fossil remains of the bones of prehistoric animals. To render these phosphates soluble they are treated with sulfuric acid.

The bones of slaughtered animals are ground and made into fertilizers. The principal mineral matter is calcium



No. Phos.	Acid Phos.	Sodium Phos.	Slag	Slag	Rock Phos.	Double Super Phos.	No. Phos.
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FIG. 189.—Effect of various phosphates on the growth of buckwheat.

phosphate. Both fish scrap and guano also contain phosphorus.

The phosphorus that is present in iron ores is removed in the slag when the iron is made into steel. This phosphate slag is a valuable source of phosphorus for use in fertilizers. Fig. 189 shows the effect of various phosphates on the growth of buckwheat. The acid phosphate, the superphosphate, and the slag are more soluble, hence of more value for immediate use. The rock phosphate shows only a little more than half the increase over the check that the acid phosphate does.

E. POTASSIUM FERTILIZERS

437. Potassium Sources. The most abundant supply of potassium is found at Stassfurt, Germany. The chlorid of potassium is the cheapest potassium compound that is available for plant food, although the sulfate is quite extensively used. The chlorid is more than 52% potassium; the sulfate contains nearly 45% potassium.

When an embargo was placed on the exportation of potash salts from Germany early in 1915 the price of potassium chlorid jumped from \$40 to \$500 per ton within a short time, and it became increasingly difficult to buy potassium compounds at all. A more intensive search was made for potassium compounds in the United States. Wood ashes contain potassium carbonate and make a good fertilizer. Some potash is obtained from the washings of wool, from plant refuse, the waste from the manufacture of sugar and molasses, and from kelp or seaweeds which were dragged ashore and burned. Beds of potash were found in California and Nebraska that yield considerable potash. Beds of rock containing potash have been located in Wyoming.

Feldspar rocks contain an abundant reserve supply of potassium. This rock weathers too slowly to meet the demand for potassium when the soil is under constant cultivation. No commercial method of rendering the potassium in feldspar immediately available is yet in use, although certain cement manufacturers are using a potassium feldspar in making cement. By the installation of Cottrell precipitators, they have recovered considerable potassium. Since the cession of Alsace to France, the German monopoly of "potash" is broken and potassium compounds are now being imported at a price lower than that charged in 1914.

SUMMARY

The process of changing *bed rock* into *mantle rock*, or soil, is known as *weathering*. If the soil remains where it was formed it is called *residual soil*.

Soils are known as *sandy*, *limy*, or *clay*, depending upon the nature of the rock from which they are formed. *Loam* is a mixture of sand and clay. Decaying vegetable matter in the soil forms *humus*.

Plants need hydrogen, oxygen, carbon, nitrogen, potassium, phosphorus, sulfur, magnesium, calcium, iron, sodium, chlorine, and silicon for growth. The first three are obtained from water and the air; the last three are less important and are generally present in all soils.

A fertile soil contains all the above elements in a form that makes them available for plant use. It should not be acid. Lime and powdered limestone are valuable for neutralizing the acidity of soils.

The elements that are apt to be lacking in a soil are *nitrogen*, *potassium*, and *phosphorus*. These may be added from time to time in the form of soluble compounds of these elements known as commercial fertilizers.

The *sources of nitrogen* include plant and animal refuse, sodium nitrate, calcium nitrate, ammonium sulfate, and calcium cyanamid.

Phosphorus for use in making fertilizers is obtained from rock phosphates, ground bone, phosphate slag, guano, and fish scrap.

Potassium is found in seaweed, wood ashes, and in feldspar rocks. Fairly extensive beds have been found in Nebraska, Wyoming, and California. Rich deposits of potassium occur at Stassfurt, Germany, and in Alsace, France.

QUESTIONS

1. How does the amount of rainfall affect the fertility of the soil?
2. Why is the soil of river bottoms so fertile? Recall the effect of the overflow of the Nile upon the fertility of the soil in Egypt.
3. How does the nature of the subsoil affect the ability of a soil to retain mineral matter to be used as plant food?
4. Why does letting a soil lie idle during the summer (summer fallow) improve its fertility?
5. Why is a loam generally a fertile soil? Would you expect a loam to be easily tilled?
6. What danger arises from too frequent addition of lime to soils?

7. What do you understand by a complete fertilizer?
8. Why is sulfuric acid used so extensively in the fertilizer industry?
9. Is powdered limestone suitable for liming soils? Is it suitable to use air-slaked lime?
10. Name as many crops as you can that may be used to enrich the soil.
11. The Indians in New England are said to have taught the early settlers to put a dead fish in each hill when planting potatoes. Would such practice be effective?
12. How are bacteria useful in enriching soils?

CHAPTER XXXVII

THE IRON FAMILY

438. Introductory. This family includes *iron*, *nickel*, and *cobalt*. From an industrial standpoint iron is the most important metal known. More than 30,000,000 tons of steel are made annually in the United States. The properties of nickel and cobalt are very similar to those of iron. The elements in this group have a valence of either *two* or *three*.

A. IRON AND STEEL

439. Occurrence. Three oxids of iron are found in nature. *Hematite*, Fe_2O_3 , is the most abundant ore. *Magnetite*,



FIG. 190.—Steam shovel used for “stripping” ores in Northern Minnesota.

Fe_3O_4 , is a little richer in iron, but it does not occur so extensively. *Limonite* is a hydrated oxid of iron and *siderite* is a carbonate. There is a large number of other iron minerals,

but nearly all the iron comes from one of the four ores mentioned.

Some iron is found near the surface and the mines are similar to quarries in the manner of operation. In Minnesota

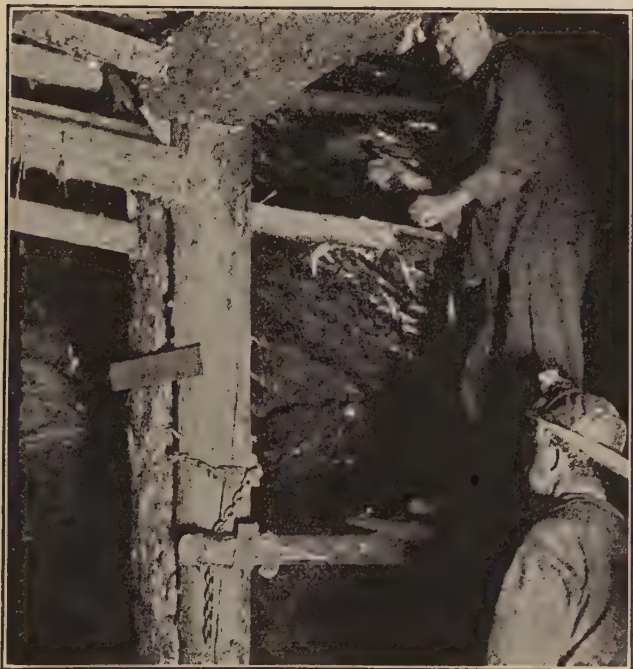


FIG. 191.—Underground or shaft mining. The loose ore must be heavily timbered.

as much as 200 ft. of earthy material is removed by “striping” to get at the ore underneath. Steam shovels are used to remove the surface layer and then load the ore thus exposed on cars for shipment. See Fig. 190. In Northern Michigan shaft mining is used, some of the ore being hoisted from a depth of nearly 2000 ft. See Fig. 191.

440. Composition, Properties, and Uses of Cast Iron, Wrought Iron, and Steel. In Chapter XXXI we learned that iron is extracted from its ores by reduction with carbon. As the iron comes from the blast furnace it contains considerable carbon and other impurities and it is known as *pig iron* or *cast iron*.

Cast iron contains from 2 to 6% of carbon, which may be chemically combined with the iron in the form of iron carbid, Fe_3C , or it may exist uncombined as graphite. If the cast iron is cooled quickly, very little of the iron carbid will decompose into iron and graphite. Such cast iron is very hard and it is white in color. Hence it is called *white cast iron*. If the cast iron is cooled more slowly it will contain more graphite. It will be softer and gray in color. It is known as *gray cast iron*. The impurities found in cast iron include phosphorus, sulfur, manganese, and silicon. Cast iron is hard, crystalline, and brittle. It is neither malleable nor ductile. It can not be tempered nor welded directly. Although cast iron is not very tenacious, it can sustain very great weights without being crushed. It melts at a lower temperature than any other form of iron, usually about 1200°C . In making castings, sand-lined molds are made into which the molten cast iron is poured and allowed to solidify.

Wrought iron is the purest form of commercial iron. It contains less than 0.3% carbon. It is made by a process known as *puddling*. This consists of heating cast iron in a reverberatory furnace (see Fig. 192) lined with iron oxid. The impurities in the cast iron are gradually oxidized and disappear as gaseous products, or they combine with the basic lining of the furnace. The molten iron is stirred until it becomes pasty, due to the fact that pure iron has a higher melting point than cast iron, and then worked into large balls called *blooms*. These blooms are removed from the furnace and worked under a trip hammer or by means of squeezers to free them from slag. Wrought iron

is soft, fibrous, ductile, and malleable. It can be welded, since it does not have a sharp melting point, but softens gradually. It can not be tempered. It is very tenacious. Since it is easily worked, it is used as blacksmith iron, for chains, and wire. Mild steel is now used extensively where wrought iron

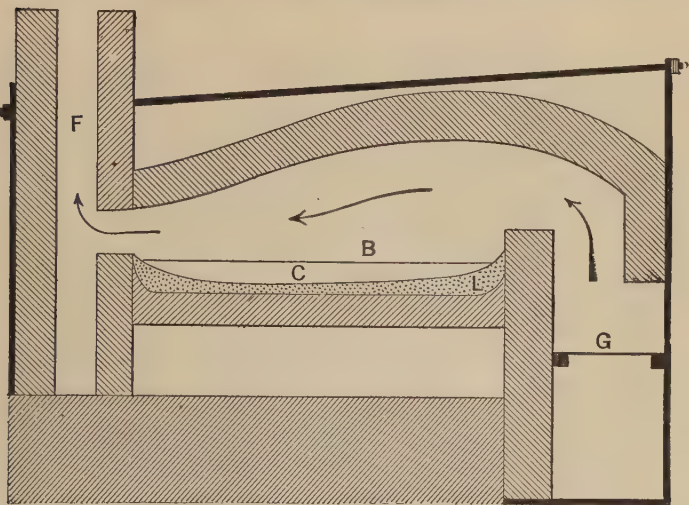


FIG. 192.—Reverberatory furnace. *G*, Grate; *C*, Charge; *L*, The lining; and *F*, The flue. Heat is reflected down upon the charge at *B*.

was formerly used. One of the largest uses for wrought iron is in the manufacture of high-grade steel.

Steel is intermediate in carbon composition between wrought iron and cast iron. It contains from 0.2 to 2% carbon. Generally its hardness increases with the increase in the per cent of carbon it contains. Steel has the highest tensile strength of the known metals. It is ductile and malleable; it can be welded and tempered. Thousands of tons are used in the manufacture of automobiles, rails, railway carriages, armor plate, guns, projectiles, bridge material, and other structural steel.

441. Manufacture of Steel. Since steel is intermediate in carbon composition between cast iron and wrought iron, it may be manufactured from either one of these substances. If it is to be manufactured from cast iron, as is more often the case, some method must be used to remove the excess carbon. If we start with wrought iron, then carbon must be



(Courtesy of the Crucible Steel Company of America.)

FIG. 193.—One of the melting furnaces used for making crucible steel.

added to give the desired percentage. Both methods are in use. The Bessemer and open-hearth processes make steel out of pig iron. Wrought iron is the material used in the manufacture of steel by the crucible process.

442. Crucible Process. In this process of making steel wrought iron, scrap steel, and carbon are heated in graphite crucibles until the melting point is reached. The temperature is then maintained until the iron has absorbed enough carbon from the graphite, coke, or charcoal introduced,

and from the crucible itself to give a steel of the desired composition. The time required is from 3 to 4 hours. As each crucible holds only about 80 lb., the process is expensive, but it yields a very high-grade product, suitable for tool steel, springs, needles, pens, and cutlery steel. See Fig. 193.

443. Bessemer Process. In this process pig iron direct from the blast furnace is poured into a large egg-shaped "converter" that holds from 10 to 15 tons. The converter is built of wrought-iron plates and lined with fire brick. The bottom contains holes through which air blasts enter in such a manner that the air finds its way up through the molten iron in many fine jets. See Fig. 194. The oxygen combines with the carbon and other

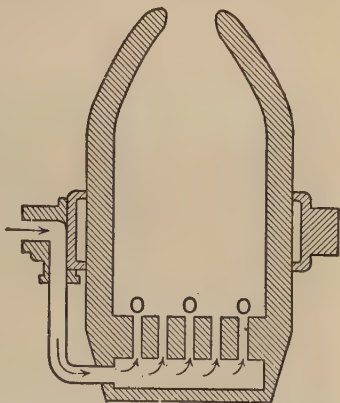


FIG. 194.—Bessemer converter, erect.

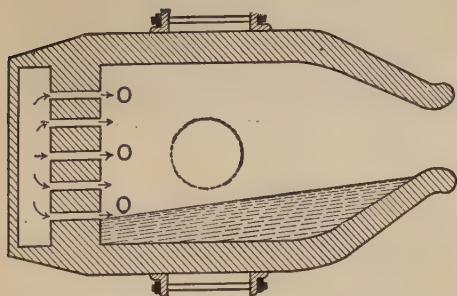


FIG. 195.—Bessemer converter, on its side

leisen mixes with the iron and forms a steel having the desired per cent of carbon. The manganese unites with the

impurities of the cast iron leaving the iron nearly pure. The blast lasts for 10 to 15 minutes. The converter is then turned down on its side (Fig. 195) and *spiegeleisen*, an iron rich in carbon and manganese, is added. The *spiege-*

oxygen and prevents the formation of "blowholes" in the steel. Fig. 196 shows a Bessemer converter in action; it affords one of the prettiest sights in modern industry.

Any considerable quantity of either sulfur or phosphorus in steel is undesirable. *Phosphorus* makes the steel brittle when

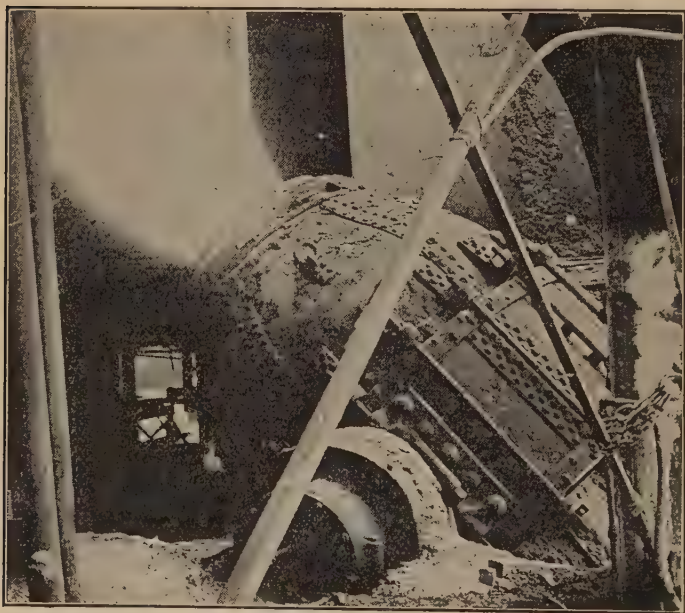


FIG. 196.—Bessemer converter in action.

it is cold; it is said to make the steel "cold-short." *Sulfur* makes the steel "hot-short," or it makes a steel brittle when hot. If steel is being made from iron which contains very little phosphorus, the converter is lined with silica. Since silica, SiO_2 , may be considered an acid anhydrid, steel made in a converter lined with this material is known as "acid Bessemer" steel.

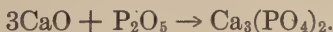
If the iron used for making steel is rather high in phos-

phorus, then the converter is lined with dolomite (CaCO_3 , MgCO_3). These carbonates when heated yield *basic oxids*, CaO and MgO . Fig. 197 shows the Bessemer converter during the various steps of its operation. The phosphorus



FIG. 197.—Sectional view of the converter at right. During the “blow” shown at center. Converter at left pouring.

is oxidized to phosphoric oxid, P_2O_5 , which combines with the basic oxids to form phosphates. For example,



This method of removing the phosphorus in a slag is known as the Thomas-Gilchrist process. The steel is sold as “basic Bessemer” steel, and the slag finds use as a fertilizer under the name Thomas slag.

444. The Open-hearth Process (Siemens Martin). The open-hearth furnace (see Fig. 198) consists of a large bed, or hearth, in which the charge, consisting of *cast iron*, *scrap*

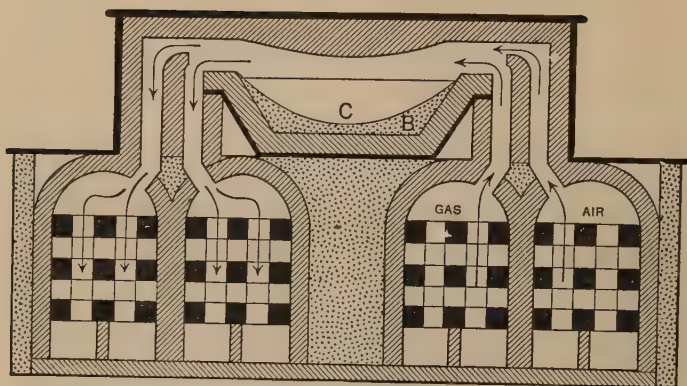


FIG. 198.—Open hearth process of making steel.

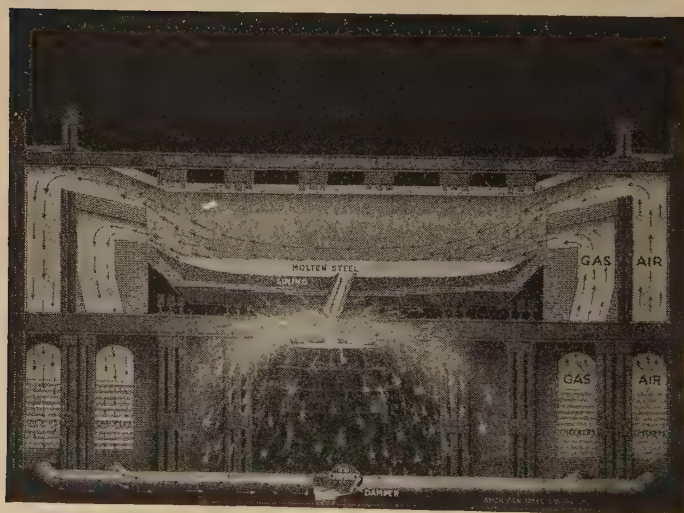


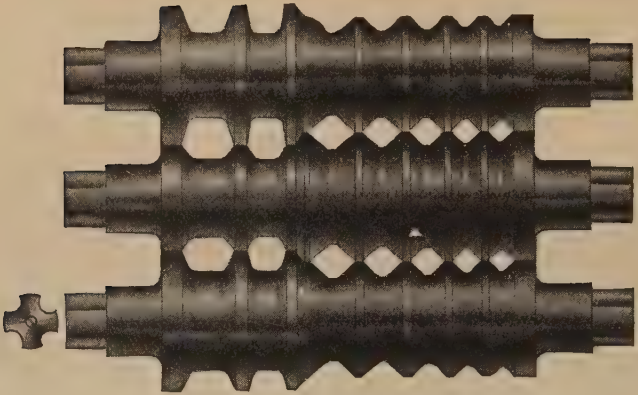
FIG. 199.—Open hearth steel pouring into ladle.

steel, and *iron ore*, is placed. The charge is heated by gas, both the gas and the air with which it combines being preheated as they enter the furnace through a checkerwork of hot fire brick. This gives a much hotter flame than could be produced by burning the cool gas. The hot products of combustion pass out through a similar checkerwork



FIG. 200.—Pouring the molten steel into the ingot molds.

on the other side of the furnace, thus heating it to a high temperature. The valves are then reversed so the gas and air may enter through the checkerwork just heated. In such a *regenerative* furnace the fuel and air enter alternately from the sides of the furnace, one side being always heated by the products of combustion as the other is being used by the entering gases. The reversal of the valves occurs about every 20 minutes. The process requires from 6 to 12 hours. Although this process requires much longer than the Besse-



(Courtesy of Scientific American.)

FIG. 201.—Roughing rolls for making bars for shrapnel.



FIG. 202.—Steel ingot about to enter rolls.

mer process, it can be better controlled, resulting in the production of a more uniform steel. The charge varies from 50 to 100 tons. Fig. 199 shows a sectional view of an open hearth furnace with molten steel and ladle. It is quite economical since the oxygen from the ore is being utilized to remove the carbon from the cast iron. Phosphorus is removed by lining the hearth with some basic material. Fig. 200 shows the pouring of ingots. The ingot is stripped, heated to the proper temperature, and then rolled into the desired shape (Figs. 201 and 202). While Bessemer steel is cheaper than open hearth, yet the great bulk of steel now made in this country is manufactured by this process.

445. Electric Process. Several types of electric furnace have been made that are suitable for making high-grade steel

out of low-grade material. In the Heroult furnace, Fig. 203, from 5 to 20 tons of material are placed on the hearth of the furnace, which is lined with some basic material to remove phosphorus and other impurities. Two carbon electrodes about 15 in. in diameter ex-

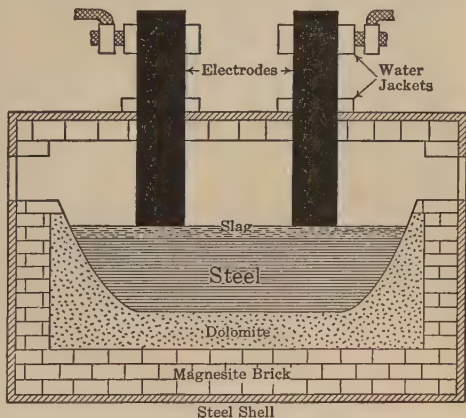


FIG. 203.—Electric furnace.

tend through the top of the furnace and dip down into the slag which is formed, but not into the iron itself. When the current is turned on, it arcs across through the slag, flows through the iron and back across the slag to the other electrode. A current of about 12,000 ampères is used in some of these furnaces. The heat produced by the current melts the

charge and its impurities are taken up by the slag. Pig iron, scrap steel, or even iron ore may be refined in such a furnace. The steel has the advantage of being made in a reducing atmosphere, and the process can be easily controlled. It requires about 3 or 4 hours to make steel in this furnace.

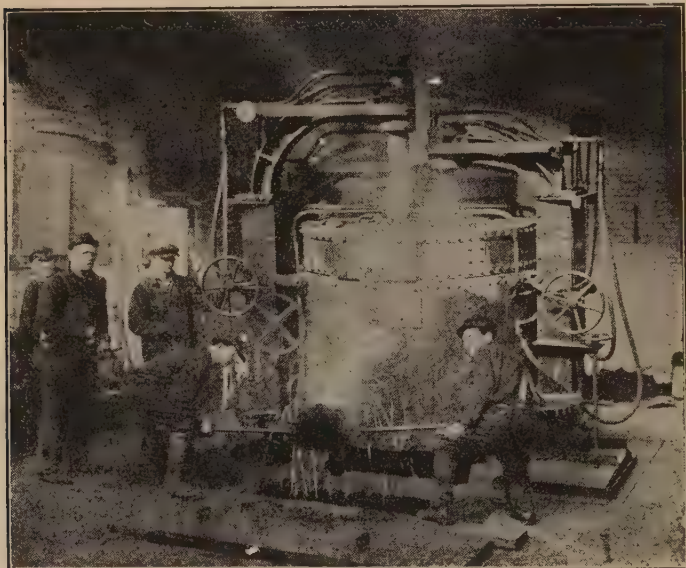


FIG. 204.—Electric furnace (pouring).

See Fig. 204. Considerable steel is made by the Bessemer process and refined in the electric furnace.

446. Purification of Steel. In making steel there is always a tendency toward the formation of oxids near the end of the process. Gases in the steel also tend to form blowholes. Both these defects are remedied by the addition of some metal that has a strong affinity for oxygen. Aluminum, titanium, manganese, and vanadium are used as *purifiers*. Titanium is especially desirable, and may be

added to the extent of 10 to 15%. It unites with both nitrogen and oxygen that may be present and gives a very homogeneous steel. The wearing qualities may be increased 40% by the use of this purifier.

447. Tempering of Steel. The properties of steel depend not only upon the per cent of carbon it contains but also upon the manner in which this carbon is held. *Mild steel* having as low as 0.2% carbon resembles wrought iron. *Low-carbon steel* contains from 0.2 to 0.8% carbon, so small an amount that it can not be tempered. *High-carbon steel* contains 0.8 to 2% carbon. It can be tempered, but it is difficult to weld.

If high-carbon steel is heated above 670° C., a carbid of iron, which goes into solution in the iron itself, is formed. If this solid solution is cooled quickly by plunging it into cold water or oil, the carbid does not separate and a very hard steel is the result. If it is cooled slowly, however, a mixture of *iron carbid*, *iron*, and *graphite* results. This product is soft and tough. All grades of hardness between these extremes may be obtained by *reheating* a hardened steel to a definite temperature and then cooling it slowly. This process is known as *tempering*. If during the re-heating the temperature is only slightly raised and the product then cooled, a very hard brittle steel is produced, since very little of the hard iron carbid separates from the solid solution. Such a steel is suitable for razor blades and cutting tools. If the solid solution of iron carbid in iron is heated to a higher temperature, 300 to 350° C., a soft, tough steel will be produced upon cooling. Such a steel is suitable for making saws and wood-working tools.

448. Special Steels. Certain metals added to steel form alloys that have special properties fitting them for particular purposes. These metals are generally added to the steel just before it is drawn from the furnace.

Nickel steel usually contains 4% or more of nickel. It does

not corrode and it combines hardness, toughness, strength, and elasticity. It finds use in making armor plate, automobile parts, and bridge material. An alloy containing a much higher percentage of nickel has the same coefficient of expansion as glass. It is used whenever wires are to be sealed in glass.

Nickel-chromium steel contains both *nickel* and *chromium*. It is very hard and tough, suitable for use as armor plate, projectiles, safes, files, plowshares, crank shafts, and gear teeth. Chromium is also used as an alloy without nickel.

Manganese steel is exceedingly hard even when cooled slowly. It is used for burglar-proof safes, jaws of stone crushers, teeth for steam shovels. It is nearly impossible to drill a hole in a manganese steel. During the war this steel was used for making helmets.

Tungsten steel contains rather a high percentage of *tungsten* and sometimes *chromium*. It may be heated to a red heat and cooled in the air without losing its temper. Hence it is known as *air-cooled*, or *self-tempering* steel. When used as a lathe tool, this steel will retain its hardness even when it is heated red hot by friction. It is often called "high-speed" steel, since it can cut about 10 times as fast as the old lathe tools. *Molybdenum* is often used instead of tungsten for making high-speed steels.

Chromium-vanadium steel has a very high tensile strength. It is used for automobile parts where the steel is subjected to severe strains and shocks. A thin strip of good vanadium steel may be bent nearly double without breaking.

Silicon steel is very flexible. It finds use in making automobile springs. It is also replacing soft iron for use in the cores of transformers and electro-magnets. A cast iron very high in silicon is not easily corroded nor attacked by acids. It is sold under the names *duriron* and *buflokast*.

449. Case Hardening. As steel increases in hardness it becomes more brittle. Quite often it is desirable to have a

steel that has a very tough core and a hard exterior. This is possible by the use of case hardening. A low carbon steel is used. When it is packed in charcoal, sodium cyanid, scrap carbonaceous material, or certain carbonates, and heated for some time carbon is absorbed at the surface. This gives a hard skin of high carbon steel on a tough core. The surface resists wear and the tough center makes the case-hardened material less liable to break.

450. Testing Steels. In the slower processes of making steel, samples of the product are taken from the furnace from time to time and sent to the chemist for analysis. Samples

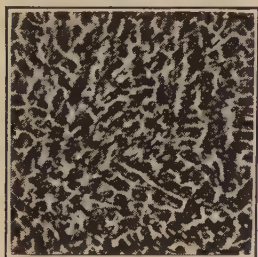


FIG. 205.—Cast iron
(100 diam.)

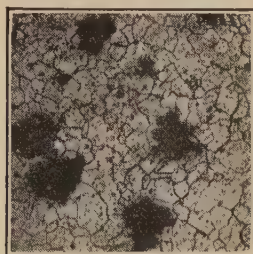


FIG. 206.—Cast iron
(annealed).

also go to the physical laboratory to be tested for hardness, tensile strength, crushing strength, and elasticity. Special tests are made when the steel is to be used for special purposes. The microscope is also used to tell what properties a steel will have. A sample is ground to give a flat surface, etched with acid, and then photographed when highly magnified. An expert in photomicrography can tell a great deal about the properties of a metal from photomicrographs. See Figs. 205–210 inclusive.

451. Properties of Iron. Pure iron is so rare that its properties have little interest for us. It is a silver-white metal, soft, tough, and ductile. It does not tarnish readily.

The iron that is used commercially varies in its properties, since it contains carbon and other impurities. All forms, however, *rust* or *corrode* in moist air. The final product is a



FIG. 207.—Wrought iron showing slag (100 diam.).

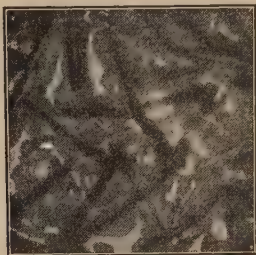


FIG. 208.—Wrought iron (reheated.)

hydrated oxid. It is probable that a basic carbonate is first formed. Iron rust is brittle and it scales off, exposing the metal underneath. Therefore *iron is not self-protective*. In fact the rust seems to act as a catalyst to form more rust,



FIG. 209.—Steel magnified (100 diam.).



FIG. 210.—Steel after reheating.

until the whole piece finally goes back to iron oxid. Acids accelerate corrosion, but alkalis retard it.

In certain cases it is quite certain that the rusting of iron is an electrical process. The carbon particles and other

impurities act as the positive plates of miniature voltaic cells. The iron is negative and goes into solution.

Dilute acids act on iron with the liberation of hydrogen. Concentrated nitric acid does not act upon iron, although dilute nitric acid acts upon it energetically. Alkalis have almost no effect upon iron.

452. Protection of Iron from Corrosion. It seems unfortunate that our most useful metal rusts so rapidly that various methods must be used to prevent corrosion. We learned when we studied zinc that the bulk of that metal is used for galvanizing iron. Iron may also be covered with a layer of tin, aluminum, or nickel.

Iron that is kept well-painted does not rust. Lacquers and enamels are surface coatings used to prevent corrosion. In making enamel-ware a special mixture of borates and silicates is fused, granulated in cold water, and then finely powdered. The iron is thoroughly cleaned and dipped into a suspension of this powder in water. It is then heated in a furnace until the powder melts to form a glaze.

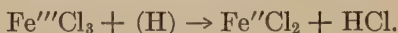
Several alloys of iron resist corrosion. Silicon alloys have been mentioned. *Stainless steel* contains from 6 to 14% of chromium. It does not tarnish. A knife made of stainless steel may be used to pare potatoes, fruits, or to cut lemons. In none of these cases is it darkened.

Iron is *Parkerized* by dipping it for a short time into a hot alkaline solution of sodium phosphate. This covers the surface with a thin coating of what is believed to be a basic phosphate of iron. The coat is so thin that the size is practically unchanged.

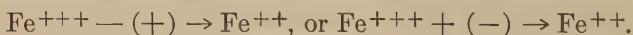
453. Oxids of Iron. Three oxids of iron are known. *Ferrous oxid*, FeO , can be prepared but it changes rapidly in the air to *ferric oxid*, Fe_2O_3 . This oxid is the most important ore of iron. It is used as a cheap red paint under the name of *red ocher*, *Venetian red*, or *Indian red*. *Rouge* is a form of ferric oxid used as a pigment and for polishing.

Limonite is a natural hydrated ferric oxid used as a pigment under the name *yellow ochre*. When calcined it forms the *siennas* and *umbers*. When iron burns in oxygen a *ferroso-ferric oxid*, Fe_3O_4 , is produced. It is black and magnetic. The scale that peels off when blacksmith iron is worked consists of this oxid. Since a thin film of this oxid is adherent, it forms a protective coat. Under the name of *Russia iron* it is artificially produced on locomotives, stoves, stovepipes, etc., to prevent corrosion.

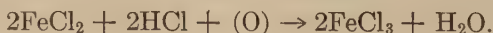
454. Oxidation and Reduction as Related to Changes of Valence. Two chlorids of iron are known: *ferric chlorid*, FeCl_3 , and *ferrous chlorid*, FeCl_2 . If we treat ferric chlorid with nascent hydrogen it is reduced to ferrous chlorid, or the valence of the iron is lowered from 3 to 2:



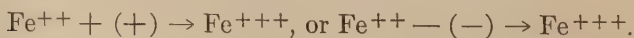
Since no oxygen is abstracted from the compound, as in the narrower sense of reduction, we may broaden the definition of *reduction* to include any chemical reaction that involves a lowering of the valence of a positive element. From the standpoint of the ionic theory, *reduction* is accomplished when an ion loses a positive charge, or gains a negative charge:



Conversely, by heating ferrous chlorid with an oxidizing agent in the presence of hydrochloric acid, ferric chlorid is produced:



In this case the valence of the iron is increased from 2 to 3. *Oxidation* may be defined as a chemical action that involves an increase in the valence of the positive element. According to the ionic theory, an ion is oxidized by gaining a positive charge or by losing a negative charge:



Ferrous salts are always formed by the action of very dilute acids since the hydrogen liberated keeps them reduced. *Ferric salts* are always formed when oxidizing agents are present. Thus moderately concentrated nitric acid always forms ferric salts.

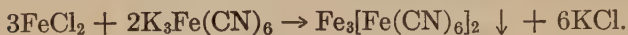
Ferric chlorid is used in medicine. Absorbent cotton dipped into a solution of ferric chlorid is known as *styptic cotton*. When put on a wound it stanches the flow of blood and also serves as an antiseptic.

455. Ferrous Sulfate. FeSO_4 . Large quantities of ferrous sulfate are obtained as a by-product by concentrating solutions used for cleaning iron and steel that is to be dipped or plated. It forms light green crystals known as *copperas* or *green vitriol*. It is used as a mordant, as a spray for destroying weeds, and in making ink.

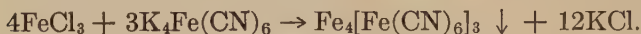
456. Inks. If we add to a freshly prepared solution of ferrous sulfate a solution of tannic acid, the nearly colorless compound, *ferrous tannate*, is formed. It slowly oxidizes to form the black compound, *ferric tannate*. Iron inks contain ferrous tannate, dextrin, some poisonous compound to prevent the growth of mold, and usually a little dye to give the ink a temporary color until the ferrous tannate is oxidized to ferric tannate to produce a permanent color. Many of the inks now used are solutions of aniline dyes. A third class of inks, of which printer's ink is a common example, is made from lampblack and some material to serve as a binder. Iron inks are easily removed by the use of a reducing agent, but the other types can not be removed by this method. Sodium hypochlorite is used extensively for removing ink stains. *It must never be used on colored fabrics or on silk*. Skimmed milk applied at once to *fresh* ink stains and then followed by cold water will usually remove nearly all the stain.

457. Tests for Iron. If we add to a solution of a *ferrous* salt a few drops of a solution of *potassium ferricyanid*,

$K_3Fe(CN)_6$, commonly called *red prussiate of potash*, a dark blue precipitate is formed. This blue substance is known as ferrous ferricyanid; it is used as a pigment under the name of *Turnbull's blue*. Since the reaction occurs only when ferrous ions are present, it serves as a test for *ferrous* iron.



A dark blue precipitate is also obtained by mixing solutions of a *ferric* salt and *potassium ferrocyanid*, $K_4Fe(CN)_6$, or the *yellow prussiate of potash*.



This reaction takes place when ferric ions are present and serves as a *test for ferric iron*. The precipitate, known as *Prussian blue*, is used as a pigment. It is sometimes used as laundry blue. If the clothes have not been rinsed free from alkaline soaps, their alkalis will decompose this blue compound, precipitating *ferric hydroxid* on the fibers and forming iron rust spots.

458. Blue-prints. Solutions of ferric salts form only a brown solution when mixed with potassium ferricyanid. Blueprints are made by coating in the dark a well-sized paper with a mixture of the solutions of *ferric ammonium citrate* and *potassium ferricyanid*. After the paper is dry it is then placed under the negative and exposed to the light. Wherever the light strikes the paper, reduction occurs and a ferrous salt is produced. The reduction proceeds more rapidly where the light is strongest. The print is developed by dipping it into water, when the *ferrous* salt formed by reduction reacts with the *ferricyanid* to form *Turnbull's blue*. Where no light strikes the print, no reduction occurs and the water washes away the unchanged mixture, thus fixing the print. The exposed portions will be blue in color and the unexposed parts will be white.

B. NICKEL AND ITS COMPOUNDS

459. Nickel. Some nickel is found in the United States, but Ontario, Canada, produces nearly all our supply. Nickel is a hard silver-white metal, capable of receiving a high polish. It does not tarnish easily. In its chemical properties nickel resembles iron, although it is not nearly so active.

460. Uses of Nickel. Considerable nickel is used as a coating to prevent the rusting of iron. Some nickel is used in hydrogenating oils, and we know that large quantities find use in making nickel steels.

The *nickel coins* are alloys containing about 20% nickel, the remaining constituents being mainly copper. *Monel* metal is made directly from a complex ore of nickel. It consists of about 67% nickel, 28% copper, and small quantities of iron and manganese. This alloy is strong and tough, and it resists the action of the air and of acids. It finds use in making valves for steam engines, and in making screens for filtering chemicals. It makes almost ideal fly screens for doors and windows. *Nichrome* is a valuable alloy of nickel, chromium, iron, and manganese. This alloy melts only at a very high temperature and it has a very high resistance to the passage of an electric current. Hence nichrome is used for making electric flatirons, toasters, and heaters. It forms excellent boxes for use in case-hardening steels.

461. Nickel Compounds. This metal forms *nickelous* and *nickelic* salts in which the valence of nickel is two and three respectively. Nickelous salts are more common; they usually crystallize as beautiful green crystals. Nickel flake and nickelous oxid are used for making the positive plate in the Edison storage battery. In charging such a battery the nickelous oxid is oxidized to the nickelic. *Nickelous ammonium sulfate* is used as the electrolyte in nickel plating.

C. COBALT AND ITS COMPOUNDS

462. Cobalt. This metal so closely resembles nickel that they are often called the twin metals. It has been used in some cases to plate iron, but it is quite expensive. The most important alloy of cobalt is *stellite*, which consists mainly of *cobalt* and *chromium*. This alloy finds use in making "stainless" cutlery, since it is very resistant to acids. It is a competitor of tungsten steel for use in lathes for cutting metals at high speed.

463. Cobalt Compounds. Like nickel and iron, cobalt has a valence of two or three. The cobaltous compounds, which exist as red crystals that form pink or red solutions are the more common. Since cobalt compounds are red when hydrated and blue when anhydrous, *cobalt chlorid*, CoCl_2 , is used as a rather crude method of determining the amount of moisture the air contains. Substances dipped in its solution change color as the moisture in the air varies. When the relative humidity is high they are pink in color; as the air grows less moist they change to a lavender or blue color. As the blue color is far more intense than the red, cobalt salts form the basis of the so-called *sympathetic* or *invisible inks*. The writing which is done with a dilute solution is almost colorless until heat is applied when the more intense blue color shows clearly. Cobalt nitrate, $\text{Co}(\text{NO}_3)_2$, finds some use in analytical work. Cobalt compounds impart to glass a beautiful blue color. A mixture of the oxids of cobalt, copper, manganese, and silver was used in gas masks during the war under the name of *Hopcalite*. This mixture was capable of oxidizing carbon monoxid, which was not appreciably adsorbed by activated charcoal, to carbon dioxid.

SUMMARY

Steel may be made from wrought iron by the *crucible* process. This process depends upon the absorption of carbon by the heated iron.

Steel is also made from cast iron by the *Bessemer* and the *open-hearth* processes. In the Bessemer process the excess carbon is all

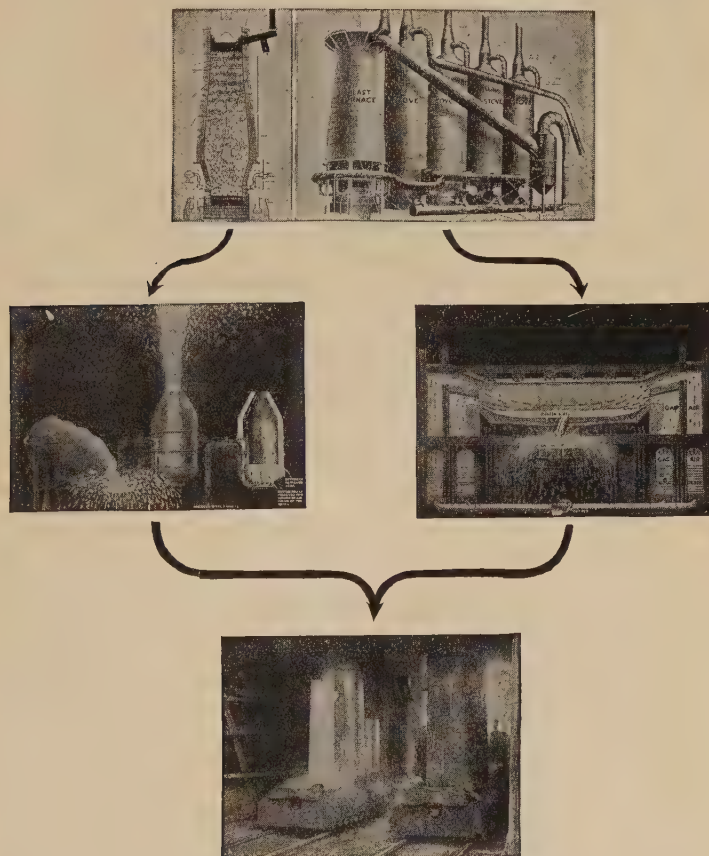


FIG. 211.—From iron ore to the steel ingot. Bessemer steel (left); open-hearth steel (right).

burned out by an air-blast, and *spiegeleisen* or *ferromanganese* is then added to introduce manganese and the proper per cent of carbon.

In the *open-hearth* process cast iron is heated with iron ore until a steel of the desired carbon content is obtained. The process is

slow enough so the product may be tested periodically. Steel is also made in the electric furnace. See Fig. 211.

When steel is heated and then cooled quickly it is very hard and quite brittle. If cooled slowly it becomes soft and tenacious. When hard steel is heated a second time to a certain temperature and then cooled properly, a process known as tempering, steel of any desired degree of hardness between these extremes is produced.

Ordinary iron rusts in moist air forming a *hydrated oxid*. Iron may be protected by covering it with zinc, tin, or nickel. Aluminum is used as a protective paint. Other methods of protecting iron include the use of lead paints, lacquers, and enamels. A thin adherent film of magnetic oxid of iron forms when iron is treated with superheated steam. Iron covered with such a protective coat is known as Russia iron. Iron or steel may be Parkerized.

Any chemical change that involves a decrease in the valence of the positive element of a compound is *reduction*. *Oxidation* causes the valence of the positive element to be increased.

Ferrous sulfate is used as a mordant, as a spray for weeds, and in the manufacture of ink.

A *ferrous* salt gives a blue color with a *ferricyanid*; a *ferric* salt gives a blue color with a *ferro-cyanid*.

PROPERTIES OF IRON AND STEEL

	Carbon content, per cent	Structure	Hardness	Properties
Cast iron.	2-6	Crystalline	Very hard	Can not be welded or tempered
Wrought iron. . .	0.05-0.3	Fibrous	Soft	Can be welded, but not tempered
Steel (low-carbon)	0.2-0.8	Granular	Moderate	Can be welded, but not tempered
Steel (high-carbon)	0.8-2	Granular	Hard	Can be welded and tempered

QUESTIONS

1. Why can not wrought iron be tempered? Why can not cast iron be welded? Why is it more difficult to weld a high-carbon steel than it is to weld a low-carbon steel?

2. Compare cast iron, wrought iron, and steel as to composition, properties, and uses.

3. What is the function of a "purifier" in steels?

4. What is meant by case-hardening? What is the purpose?

5. Why would you not expect to find iron occurring free in nature?

6. Freshly prepared ferric hydroxid is an antidote for arsenic poisoning. How would you prepare this compound? Write the equation for the reaction.

7. How would you convert ferric chlorid into ferrous chlorid?

8. What would happen if you added some hydrogen peroxid to a solution of ferrous sulfate?

9. Oxalic acid is a reducing agent. What kind of ink stains can be removed by the use of oxalic acid?

10. Which class of iron compounds is more stable when exposed to air? Which would be more stable, the *dry* salts or their *water solutions*?

11. How would you remove a stain made with an iron ink? Would the same method be useful for removing rust stains made in the laundry from Prussian blue?

12. If you were given an iron solution how would you tell whether it contains ferrous or ferric iron?

13. Given a solution of an iron salt. How could you tell whether it is a chlorid, a nitrate, or a sulfate?

14. Name three important alloy steels, giving their uses.

15. How are sympathetic inks used?

16. Name as many ways as you can of protecting iron from corrosion.

17. What kind of iron ore is made into steel by the *acid* Bessemer process?

18. Give two definitions of oxidation. Two of reduction.

PROBLEMS

1. How many pounds of iron can be obtained from one ton of ore that is 95% hematite, Fe_2O_3 ?

2. How many pounds of iron chlorid can be made by dissolving 500 lb. of iron in hydrochloric acid?

3. How many pounds of iron nitrate can be made by dissolving 500 lb. of iron in dilute nitric acid?

4. A lump of iron weighing 112 gm. is dissolved in hydrochloric acid. How many grams of ferrous chlorid will be formed? How many liters of hydrogen will be set free?

CHAPTER XXXVIII

THE COPPER FAMILY

464. Introductory. The copper family includes the metals copper, silver, and gold. All of these metals are found free in nature to some extent. They are all soft, heavy metals, both ductile and malleable. They form the best conductors of heat and electricity known. All the metals are quite inactive chemically. The valence of the family is one, but copper is more often two, and gold is usually three.

A. COPPER

465. Occurrence. About 60% of the world's annual output of copper is produced in the United States. In Northern Michigan copper is found native, sometimes in large masses six feet thick. See Fig. 212. Usually it is mixed with quartzite rock. The sulfids of copper are found in Montana. *Chalcocite*, Cu_2S , is known as copper glance. Two double



FIG. 212.—Mass of native copper.

sulfids of iron and copper, *chalcopyrite* and *bornite*, are important ores. In Arizona copper occurs in the form of two beautiful minerals, *malachite* and *azurite*. Both are basic carbonates of copper. Gold and silver, together with arsenic and antimony, are usually found associated with copper ores.

466. Extraction of Copper. The sulfid and carbonate ores are first roasted to form the oxid of copper which is then reduced with carbon. In the reduction of the complex sulfids of iron and copper, the process is more complicated and a product known as *matte* is first formed. A preliminary roasting partially oxidizes the sulfids. The *roasted ore*, *some unroasted ore*, and *coke* are then heated in a blast furnace similar to that used in the extraction of iron. A matte consisting largely of cuprous sulfid, with traces of gold, silver, arsenic, and antimony is formed in the furnace. The bulk of the iron unites with the silica used to line the furnace and forms a slag. Both the slag and the matte are then drawn off into a forehearth. The lighter slag floats and is removed from the top of the hearth, while the matte is drawn off at the bottom. In this manner nearly all the iron is separated from the copper.

467. Making Blister Copper. The *matte* is poured into a converter which does not differ essentially from the converter used in making Bessemer steel. Here the sulfur, arsenic, and antimony are oxidized and volatilized by the air-blast. See Fig. 213. Any iron that remains combines with the silica used to line the furnace and forms a slag. After the copper is poured from the converter, it expels in cooling some sulfur dioxid which had been absorbed. The product is full of bubbles and is known as "blister" copper. The silver and gold are still retained by the copper.

468. Poling Copper. Blister copper contains traces of copper oxid which may be removed by a method known as *poling*. The melted blister copper is stirred in a reverberatory furnace with long green poles. Hydrocarbons escape

from the pole and reduce the copper oxid to copper. The poled copper is then cast into anode plates to be refined by electrolysis.

469. Refining of Copper. For two reasons copper is refined before it is put on the market. 1. Appreciable amounts of gold and silver are left in the poled copper.

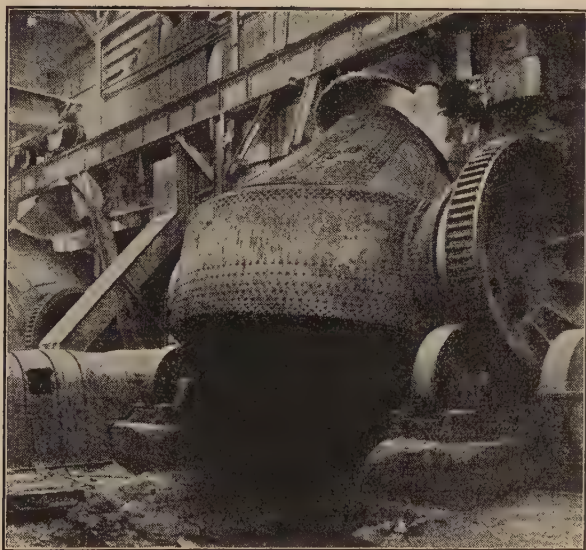


FIG. 213.—Converter used for making blister copper.

2. Copper is largely used for making electrical conductors, and small amounts of impurities increase its resistance. Traces of arsenic in copper lower its conductivity decidedly. As low a percentage of iron as 0.4 of 1% decreases the conductivity of copper 64%.

In refining copper, sheets of pure copper form the cathodes and large plates of impure copper the anodes. The electrolyte is a solution of copper sulfate in sulfuric acid. Copper goes into solution at the anode and *pure* copper is deposited

at the cathode. See Fig. 214. The impurities fall to the bottom of the tank as a mud or slime. The gold and silver are recovered from this slime. Fig. 215 shows the rotating table upon which copper ingots are cast in molds.

470. Properties of Copper. Copper is a soft, red metal. It is ductile, malleable, and very tenacious. Its specific

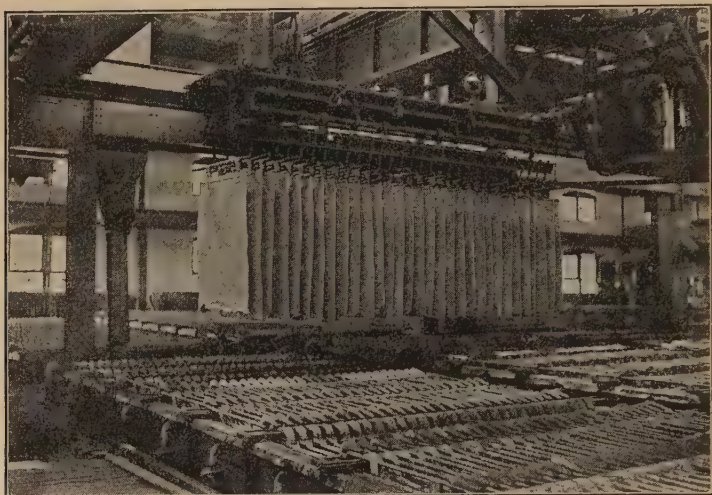


FIG. 214.—Refining copper by electrolysis. A set of electrodes lifted from the electrolytic tank is shown at center.

weight is 8.9. As a conductor of heat and electricity, copper stands next to silver.

Heated in the air, copper forms the black *cupric oxid*, CuO ; its vapor burns with a green flame. Exposed to the action of sulfur fumes, copper soon becomes covered with a blue-black coating of copper sulfid, CuS . Copper tarnishes in moist air, a green basic carbonate often being produced. It is self-protective as the tarnish is adherent. Hydrochloric acid does not affect copper, nor does dilute sulfuric. Nitric acid and hot concentrated sulfuric acid, acting as

oxidizing agents, attack copper forming the nitrate and sulfate respectively. The soluble compounds of copper are poisonous.

471. Uses. Copper is extensively used for making electrical conductors. It also finds use for sheathing ships, for making electrotypes, and in several alloys.

Brass is an alloy of copper and zinc; *bronze* contains tin in addition to these elements; *German silver* contains copper,

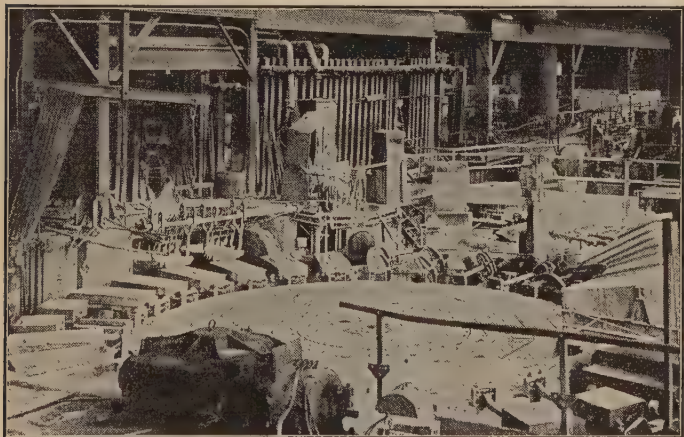


FIG. 215.—Molds in which copper ingots are cast.

zinc, and nickel. All the coins contain some copper, the copper coins as high as 95%.

472. Compounds. Copper forms *cuprous* and *cupric* compounds. In *cuprous oxid*, Cu_2O , the valence is 1; in *cupric oxid*, it has a valence of 2. The cupric compounds are the more important. *Copper sulfate*, CuSO_4 , is the most important compound of copper. It forms large blue crystals having the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It is generally known as *blue vitriol*, or *bluestone*. Copper sulfate finds use as a mordant in calico printing, in voltaic cells; for copper plating and

electrotyping, and as a fungicide and insecticide. For spraying fruit trees and grapevines, it is generally used in the form of *Bordeaux mixture*, a preparation made by mixing a solution of copper sulfate with slaked lime. This preparation was first used in the vineyards of France to prevent mildew. It has been found to be effective in spraying potato vines in efforts to check blight. We have already learned that copper sulfate is used for destroying algæ in city reservoirs.

B. SILVER

473. Occurrence. Silver is sometimes found free in nature. The ores of silver include the *sulfid*, Ag_2S , and the *chlorid*, AgCl . We have learned that silver is commonly associated with copper ores and similarly many lead ores are silver-bearing. The United States, Mexico, Canada, and South America are the largest producers of silver.

474. Extraction. The anode "mud" left in the refining of copper is screened and then treated with sulfuric acid. The silver goes into solution as silver sulfate. Copper is then added to precipitate the silver.



In the Parkes' process of recovering silver from argentiferous lead ores the lead sulfid is roasted and treated as described in section 489. Then the lead, which contains both silver and gold, is heated in a reverberatory furnace. Such impurities as arsenic, antimony, etc., are oxidized and skimmed off the surface of the molten lead. Pieces of zinc are then added to the lead, which is stirred in large kettles. The gold and silver form an alloy with the zinc and are thus separated from the lead. This alloy is lighter than lead and is removed as it floats at the top of the kettle. See Fig. 216. The zinc is recovered by heating this alloy, which also contains some lead, in a retort. The zinc distils off, and is

condensed for further use. The lead remaining is separated from the gold and silver by heating the residue left in the retort in bone-ash or cement *cupels*. Part of the lead is oxidized and a part is absorbed by the cupel. The silver is then



FIG. 216.—Kettles for desilvering lead.

dissolved by the use of hot sulfuric acid and reprecipitated by the addition of copper or by electrolysis.

475. Properties of Silver. Silver is a soft, white, lustrous metal. It is very ductile and malleable. Its specific weight is 10.5. Of all the metals silver is the best conductor of heat and electricity.

Silver is an inactive metal, since it does not oxidize even in moist air. If the air contains traces of sulfur, however, a brownish-black tarnish of *silver sulfid* is readily formed. Silver dissolves readily in nitric acid and in hot concentrated sulfuric. Hydrochloric acid does not attack it, nor does dilute sulfuric acid.

476. Uses. Silver is used in jewelry and coins. The U. S. silver coins contain 90% silver and 10% copper. The British coins contain 92.5% silver. *Sterling silver* is an

alloy having the same per cent of silver as the British coins. Large quantities of silver are used for plating tableware. In silvering mirrors, advantage is taken of the fact that silver compounds are easily reduced, the silver being deposited on the glass as the reduction occurs.

477. Silver Compounds. *Silver nitrate*, AgNO_3 , crystallizes in colorless scales. Under the name of *lunar caustic* it is sometimes used by surgeons for cauterizing abnormal growths. *Oxidized silver* is a sulfid of silver made by dipping the metal into a solution of a sulfid, usually of sodium or ammonium. *Silver chlorid*, AgCl , *silver bromid*, AgBr , and *silver iodid*, AgI , are all sensitive to light when organic matter is present. The action is one of reduction, the metallic silver that is formed being finely divided and dark in color. These compounds are used in photography.

478. Photography. The main steps in the chemistry of photography consist: (1) in preparing the negative; (2) in making the print. In the preparation of the negative there are three important operations: (1) *the exposure*; (2) *developing*; (3) *fixing*. The plate used for making the negative is prepared by covering a glass plate or celluloid film with gelatin containing silver bromid in suspension. This plate is *exposed* to the light just long enough to start the reduction of the silver bromid. It is then treated in a dark room with a *developer*, which consists of rather mild reducing agents, such as hydroquinone or pyrogallol. The developer can not start the reduction of the *unchanged* silver salt, but it can continue the reduction begun by the action of the light. After the developing process has proceeded far enough, the plate or film is then put into a strong solution of sodium thiosulfate, commonly known as *hypo*. This solution dissolves the unchanged silver salt so the plate will not darken when again exposed to the light. The "hypo" thus serves as a *fixer*. The more intense the light the more

rapidly the reduction occurs. White reflects more light than colored objects, hence white objects make the plate very



FIG. 217.—A negative plate.

dark and *vice versa*. For these reasons the plate is now called a *negative*. See Fig. 217.

In making the print, a well-sized paper sensitized in the

same manner as the plate, is covered by the negative and then so exposed that the light must pass through the nega-



FIG. 218.—A positive print.

tive. Here the dark part of the negative cuts off the more light and the intensity of reduction is just the reverse from that in the production of the negative, and a positive print

is produced. See Fig. 218. The print is developed and fixed in the same manner as the plate. It is often *toned* by dipping it into a solution of the salts of gold or platinum. The silver goes into solution replacing these metals which are thus deposited on the print in place of part of the silver. Gold gives warmer tones than silver. Platinum produces a purplish color, or even a black. Sometimes the silver is partially oxidized and then converted into a sulfid to produce a sepia print.

C. GOLD

479. Occurrence. We have already seen that gold is obtained from the ores of lead and copper. It is also found *native*, either in fine particles mixed with sand, or in veins of quartz. It can be profitably extracted when the quartz contains only a fraction of an ounce per ton of material.

480. Extraction. When the gold occurs in *alluvial sand* deposits, hydraulic mining is used. Streams of water directed against the deposits carry away the earthy material through sluices. The heavy gold falls to the bottom where it is retained by riffles.

Gold-bearing quartz ores are crushed to a fine powder by the use of a stamp mill. As the powder is carried away by water it comes into contact with mercury, which forms an amalgam with the gold. The gold amalgam is then distilled to recover the mercury.

From certain ores gold is extracted by treating them with moist *chlorin* gas. The gold is dissolved by the chlorin, forming *auric chlorid*, AuCl_3 . Ferrous sulfate serves as a reducing agent to precipitate the gold.

Low-grade ores are treated with *sodium cyanid* in the presence of air. The gold goes into solution as a double cyanid of sodium and gold, from which the gold can be precipitated by the addition of a metal or by electrolysis.

481. Properties and Uses of Gold. Gold is a soft, yellow metal, very ductile and malleable. It has been hammered out into sheets so thin that it would take about 250 of them to make a sheet as thick as a leaf of paper in this book. Gold is a good conductor of heat and electricity. It is a very heavy metal, its density being 19.3. It is about 7 times as heavy as aluminum and nearly twice as dense as silver. Gold does not tarnish when exposed to the air; it is a very inactive metal. No single common acid affects gold, but it dissolves quite readily in aqua regia.

Gold finds use in making coins and jewelry. Since it is too soft to wear well, it is usually alloyed with copper. Its purity is expressed in *carats*, pure gold being 24 carats fine. Eighteen-carat gold contains 75% gold and 25% copper. Gold coins contain 90% gold.

482. Compounds of Gold. In *aurous* compounds gold has a valence of one; its valence is more often three, in *auric* compounds. *Auric chlorid*, AuCl_3 , is one of the most important compounds of gold. It is used in photography. A double cyanid of gold and potassium is used in gold plating.

SUMMARY

The *sulfids* and *carbonates* of copper are important ores. Copper also occurs *native*. The ores of copper are roasted, and then reduced with carbon. Copper is generally refined by electrolysis.

Copper is a heavy, ductile metal used extensively for electrical conductors. It is a self-protective metal. Nitric acid attacks copper readily.

Copper sulfate is used in batteries, for copper plating, for water purification, and as a fungicide and insecticide.

Silver is the best conductor of heat and electricity known. It is used in jewelry, in silver coins, and for plating tableware.

Silver salts are sensitive to light. Thus they find use in photography. Two important steps in photography consist: (1) in making the negative; (2) in making the print.

In making a negative there are three operations: (1) the exposure, which starts the reduction of the silver salt; (2) the develop-

ing, which continues the reduction; and (3) the fixing, which removes the unchanged silver salts and makes the negative permanent.

The same operations are used in making the print; it is frequently toned by replacing the silver on the print with gold or platinum.

Gold is mined by the *hydraulic* or by the *amalgamation* process. It is often extracted by dissolving the gold with *chlorin* or with *sodium cyanid*.

Gold is a valuable yellow metal. It does not tarnish; hence it is suitable for use in making coins and jewelry. Pure gold is 24 carats fine.

QUESTIONS

1. Why is copper not suitable for making cooking utensils?
2. If dilute sulfuric acid does not act on copper, explain how copper sulfate can be made by putting copper shot in a lead basket and alternately dipping them in warm dilute sulfuric acid and then suspending them in the air.
3. How could scrap iron be used to recover copper from the waste waters of copper mines?
4. How could you tell gold from brass?
5. By the aid of a labeled diagram, outline a method of plating tableware with silver.
6. What is Bordeaux mixture? For what purpose is it used?
7. Why must copper be so highly purified?
8. How is iron separated from copper in the complex copper-iron sulfids?
9. Why is silver-plated ware more easily scratched than sterling silver?
10. What causes eggs and mustard to tarnish silverware?
11. Tarnished silverware may be cleaned by putting it in an aluminum dish containing boiling water and a little baking soda. Explain.
12. Which forms the better coating for mirrors, silver or tin amalgam? Give two reasons for your answer.
13. What is "oxidized" silver?
14. Outline the various steps from the time a photographic plate is exposed until the print is finished.
15. Why should gold rings not be permitted to come into contact with mercury?
16. How can gold be recovered from gold chlorid?
17. How could you make colloidal gold? What use is made of colloidal suspensions in photography?

18. Can you give a reason why indelible inks often contain silver salts?

19. Sodium and potassium are both widely distributed, but they are comparatively new metals. On the other hand, copper, silver, and gold were known to the ancients. Explain.

CHAPTER XXXIX

TIN AND LEAD

483. Introductory. To some extent tin and lead resemble carbon and silicon. They differ from these elements, however, since they may act as metals. While *stannates* and *plumbates* are known, yet both tin and lead generally act as metals in chemical reactions. Tin has a valence of either two or four. Lead is usually two, although oxids are known in which its valence is one, three, or four.

A. TIN

484. Occurrence and Extraction. The chief ore of tin is the oxid, *cassiterite*, SnO_2 . It is often known as tin stone.



FIG. 219.—Blast furnace for reduction of tin.

England has long been a producer of tin. Rich ores are found in the East Indies and in Bolivia.

Tin ores are very easily reduced by heating with carbon. Fig. 219 shows the tapping of a blast furnace in which tin is reduced. The metal is now refined by electrolysis. See Fig. 220.

485. Properties of Tin. Tin is a soft white metal, a little lighter than iron. It has a very low melting point, 232° C. The pure metal is known as *block tin*. It is so malleable that it may be rolled into very thin sheets, known as *tin foil*.

Air and water do not act on tin at the ordinary temperature. Dilute acids have little effect on tin, but concen-

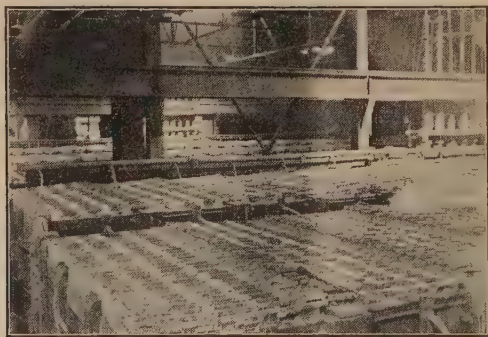


FIG. 220.—Tank house for the electrolysis of tin.

trated acids attack it readily. With hydrochloric acid it forms stannous chlorid. Sulfuric acid forms a sulfate of tin. The action of nitric acid on tin is very peculiar. Instead of a nitrate being formed the tin is oxidized to form *metastannic acid*, H_2SnO_3 , a white insoluble compound. In cold climates tin changes to a brittle gray powder. This is an allotropic form of tin. This crumbling of tin in cold weather is sometimes spoken of as “tin disease.”

486. Uses of Tin. Ordinary *tinware*, or *tin plate*, is made by cleaning sheet iron and dipping it into molten tin. Such tinned iron is used for making “tin” cans and cooking

utensils. If the coat is thick enough it does not rust, but the iron rusts very rapidly as soon as the coating of tin is broken at any point, since the contact of two metals causes the more active one to corrode very rapidly. In reality, a voltaic cell is formed in which the tin is positive and the iron negative. Thus the iron goes into solution. When zinc



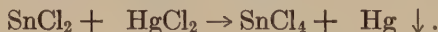
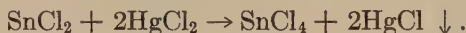
FIG. 221.—The iron is carefully cleaned, dipped into melted tallow and then into a vat of molten tin in the making of tinware.

is used to protect iron, it affords protection even after the coating has been broken. In this case, the zinc is negative with respect to the iron. The positive iron is protected as the zinc goes into solution. For this reason zinc is sometimes spoken of as a "sacrificial metal." *Tin foil*, especially the cheaper grades, often contains some lead. Pure tin pipes are used as conduits for slightly acid liquids.

Solder is an alloy of tin and lead. It varies in composition,

a soft solder containing a higher percentage of tin than a hard solder. Plumbers use a solder containing 67% of lead for wiping joints, since such a solder becomes plastic before it cools enough to grow hard. Other alloys of tin, such as bronze, type-metal, anti-friction metals, and fusible metals, have already been studied.

487. Compounds of Tin. *Stannous chlorid*, SnCl_2 , is an important compound of tin. It is used as a mordant, since it forms very brilliant shades. Stannous chlorid is also used for weighting silks. It is a reducing agent. An interesting example of oxidation that does not involve a transfer of oxygen occurs when a solution of stannous chlorid is added to mercuric chlorid:



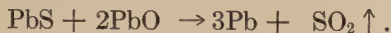
In these interactions stannous chlorid acts as a reducing agent. The mercuric chlorid acts as an oxidizing agent. Stannic chlorid, SnCl_4 , in which tin has a valence of 4, is formed and the bichlorid of mercury may be reduced to the mono-chlorid or to the metallic state. *Stannic sulfid*, SnS_2 , is used as a yellow pigment under the name of "mosaic gold." Metastannic acid is used to strengthen cotton fibers and to render them non-inflammable.

B. LEAD

488. Occurrence. The most important ore of lead is *galena*, or lead sulfid, PbS . It is found as cubical, grayish-black crystals. In the United States lead is found in Missouri, Illinois, and Colorado. It occurs abundantly in Canada and Mexico.

489. Extraction. If the ore is free from siliceous matter, it is first roasted at a low temperature in a reverberatory furnace. This converts part of the lead sulfid into the oxid,

PbO, and the sulfate, PbSO₄. When the temperature is then raised the following reactions occur between the unchanged lead sulfid and the oxidized products:



Low-grade ores, and those containing silica are reduced in a blast furnace with carbon. Lead may be cast into anodes and purified by electrolysis.

490. Properties. Lead is a soft bluish-white metal. Its specific weight is 11.3, it being heavier than most of the common metals. Lead is malleable, but not ductile. It may be made into wire, however, by forcing the heated metal through a die. Lead pipe is made in a similar way by forcing the metal through a ring-shaped opening.

Lead oxidizes quite rapidly, but the coating is adherent and protects the metal underneath. Hydrochloric acid and sulfuric acid have little effect on lead, but nitric acid acts upon it vigorously. Acetic and other organic acids act readily on lead, and water containing carbon dioxid acts upon it slowly. *As all soluble lead compounds are poisonous*, lead is objectionable for use in making water pipes. Lead salts are especially dangerous even in small quantities as they are not readily excreted, but accumulate in the body. Painter's colic is a disease due to chronic lead poisoning.

491. Uses. Enormous quantities of lead are used in making white lead paint. Sheet lead is used for lining the chambers of sulfuric acid plants and for the plates of storage batteries. Lead pipe is used as conduits for electrical wires; plumbers also use lead pipe since it is easy to cut, it may be readily bent into any desired shape, and its edges may be readily fused or soldered together to make a seamless joint. Lead foil is used for lining tea chests, and as a substitute for tin foil. Except for its weight, sheet lead makes excellent roofing material.

Shot is made from lead containing a trace of arsenic. The other alloys of lead, solder, type-metal, fusible metals, and antifriction metals, have been studied under other titles.

492. Oxids of Lead. Three oxids of lead are important: *Lead monoxid*, PbO , commonly known as *litharge*, is a yellow powder used in the glass, paint, and varnish industries. *Lead dioxid*, PbO_2 , is a brown powder used as an oxidizing agent. It is formed when storage batteries are charged,



FIG. 222.—Lead disc.

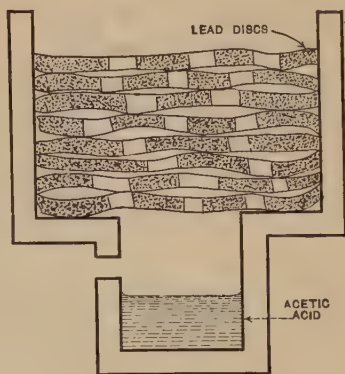


FIG. 223.—Pots containing lead discs.

and becomes the positive plate. *Red lead*, or *minium*, is an oxid of lead having the formula Pb_3O_4 . It is used as a red pigment. Mixed with linseed oil it serves as an oxidizing agent, causing the oil to dry or harden rapidly.

493. White Lead. Several processes are in use for making white lead. The Dutch process has been in use for centuries and yields a very good product. In this process perforated lead discs (Fig. 222), or "buckles," are placed in earthenware pots containing a little dilute acetic acid. See Fig. 223. The pots are then placed in rows and covered with stable manure or with spent tan bark. Other tiers of pots are placed on the first ones and covered as before, until a

considerable height is reached. See Fig. 224. The heat from fermentation vaporizes the acetic acid which acts on the lead to form a basic lead acetate. Carbon dioxide which is liberated by the fermentation changes the acetate into a *basic lead carbonate*. The process requires 90 days or more. The aim is to produce a white lead having the formula $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, but the product varies to some extent. Fig. 225 shows workmen removing the corroded buckles from the pots. White lead is ground very fine with linseed oil and used as a paint base.

In the Carter process melted lead is atomized by a blast of steam and the fine powder is treated with carbon dioxide in a rotating cylinder. The lead is kept moist and acetic

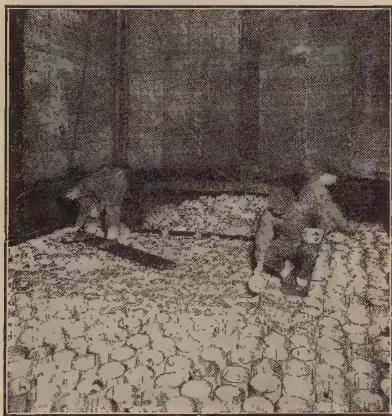


FIG. 224.—Placing lead buckles in pots for making white lead.

acid is sprayed into the cylinder at intervals. It requires about two weeks to make white lead by this process.

494. Other Lead Compounds. *Lead acetate*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is a white crystalline solid commonly known as *sugar of lead*. Like other *soluble lead compounds*, it is *highly poisonous*. It finds some use as a mordant, and it is sometimes applied externally in cases of ivy poisoning. *Lead chromate*, PbCrO_4 , is a pigment usually called *chrome yellow*. *Sublimed white lead* is used as a paint base. It is made by roasting galena, which contains some zinc, at a high temperature. The finished product consists of lead oxide, lead sulfate, and zinc oxide.

C. PAINTS

495. Paints. A paint consists of: 1, a *paint base*; 2, a *vehicle*. It may also contain a *colored pigment*. A good paint base should be opaque even when it is spread out in very thin layers; it should mix readily with the vehicle, which is

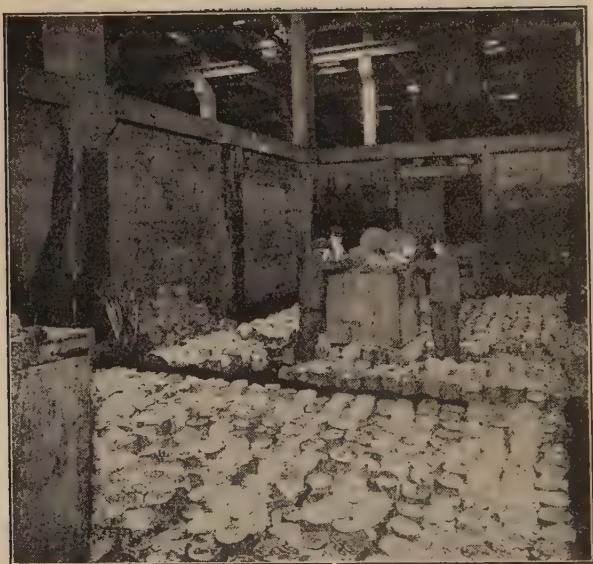


FIG. 225.—Removing the corroded buckles.

an oil that “dries” and forms a skin to hold the base; it should be durable.

White lead answers all these requirements remarkably well, but it has a tendency to become chalky with age. It is also poisonous when it finds its way into the body. Its use has been forbidden in France. It becomes black when used in places where it comes in contact with hydrogen sulfid. It works well under the brush and it has great covering power.

Zinc oxid does not have so good a covering power as white

lead. It tends to peel off or scale if used alone. It does not turn black when exposed to hydrogen sulfid, since zinc sulfid is white. Hence it is used as an *inside* white. It is whiter than white lead. When these two paint bases are mixed, each has a tendency to counteract the defects of the other.

Sublimed white lead is coming into favor as a paint base. It is not affected by sulfur vapors, and it is less poisonous than white lead. It is very durable and it has good covering power.

Lithopone is a paint base made by treating zinc sulfate with barium sulfid:



The mixture of *zinc sulfid* and *barium sulfate* formed by the above reaction does not make a good paint base. It is calcined first at a red heat and then plunged into cold water. Later it is ground in oil to make it a paint base. *Lithopone* is very white, and it has good covering power. It darkens upon exposure to light, hence it is used for inside work or as an undercoat for enamels. It also finds use as a filler in the rubber industry.

496. Vehicles. *Linseed oil* is the vehicle most often used in paints. It is an *unsaturated* compound that "dries" by uniting with oxygen from the air to form a tough resin. The leathery skin seen on the surface of a ready-mixed paint that has stood for several days is an example. This resin, which is known as *linoxyn*, holds the paint base in place when a paint "dries." *Boiled linseed oil* is made by heating the raw oil with oxids of lead or manganese. This treatment makes the oil harden or "dry" more rapidly.

Chinese wood oil is used as a vehicle in some enamel paints and in other paints that are to be subjected to very severe weather conditions. *Rosin oil* is sometimes used to adulterate linseed oil. It has some drying properties. Such a mixture is called "sipes" oil by painters.

The "driers" used in paints are made by heating a part of the oil with oxids of lead and manganese. They act as catalytic agents, giving up a part of their oxygen to hasten the hardening of the oil and subsequently absorbing oxygen from the air.

Such liquids as turpentine, alcohol, and mineral oils (called "painter's spirits") are not vehicles. They serve as solvents and thinners or diluents. They dry by evaporation.

497. Pigments. A pigment is some insoluble substance of high coloring power that is added to a paint base. A large number are used and their composition varies greatly. They include lakes, oxids and sulfids of metals, complex cyanids, etc. Chromium compounds are especially valuable as pigments.

Red pigments include red lead, red ocher, vermilion, and carmine, compounds already studied.

Blue pigments include such compounds as Prussian blue, ultramarine, and cobalt blue.

Yellow pigments include chrome yellow, yellow ocher, and litharge.

From mixtures of these pigments and others not given here, the various shades may be produced.

498. Extenders or fillers are used in paints, especially in ready-mixed paints. They are cheaper substances than the paint bases and are often classed as adulterants. They often increase the durability of the paint, and they so completely fill the pores that the surface is more easily repainted. Kaolin, barium sulfate, calcium sulfate, and whiting, or calcium carbonate, are some of the most common fillers.

SUMMARY

Tin is a soft, white, malleable metal. It does not tarnish in the air. Acids act upon it rather readily.

Tinware is sheet iron covered with a coating of tin. Tin foil finds considerable use as air-tight wrapping material.

Solder contains tin and lead. Other alloys of tin are *bronze*, *type-metal*, and *antifriction metal*.

Stannous chlorid is used as a mordant and for weighting silks.

Lead is a soft, bluish-white metal. Exposed to the air it soon becomes covered with a protective layer of the *oxid*, Pb_2O . Nitric acid and organic acids act readily on lead. *Lead salts are very poisonous*. Epsom salts forms a good antidote.

Lead is used for making paints. It is also used for making pipe, and as sheet lead. Shot, solder, type-metal, and the fusible alloys contain lead.

Litharge, PbO , and *minium*, Pb_3O_4 , are oxids of lead used in the paint industry. *Lead peroxid*, PbO_2 , is used in storage batteries.

White lead is a *basic lead carbonate* that is used as a paint base. *Sublimed white lead* contains lead sulfate, lead oxid, and zinc oxid. *Chrome yellow* is a chromate of lead.

A paint consists of a paint base mixed with a vehicle. The most common paint bases are white lead, zinc white, mixtures of these two substances, sublimed white lead, and lithopone. The most common vehicles are linseed oil and Chinese wood oil.

A pigment is a highly colored substance sometimes added to a paint base to give it some desired shade or color. An *extender* is a cheap product often added to ready-mixed paints. They are often classed as adulterants, although they may increase the durability of the paint.

QUESTIONS

1. Which makes the better coating for iron, tin or zinc? Give a reason for your answer.

2. How could tin be recovered from tin cans?

3. Tinware rusts rapidly as soon as a little of the iron is exposed. Explain.

4. Write the equation representing the reaction between solutions of stannous chlorid and auric chlorid.

5. Solutions of stannous chlorid do not keep well when exposed to the air. What two changes may occur? How does the addition of a little metallic tin and hydrochloric acid aid in preserving such a solution?

6. What is the chief objection to the use of lead as a roofing material?

7. Can you see any reason why some countries restrict the manufacture and use of white lead?

8. Compare zinc white and white lead as paint bases.

9. Would you use white lead in a laboratory or a kitchen? Give a reason for your answer.

10. How could you use a solution of lead acetate to test for the presence of hydrogen sulfid in illuminating gas?

11. An American chemist won a prize for a method of restoring the color to some valuable paintings that had been darkened by sulfur vapors. He washed the paintings with hydrogen peroxid. Explain the chemical action.

12. What is the function of "driers" in paints? Of extenders? Of diluents? Of the vehicle?

13. What are the advantages and disadvantages of tin plate for roofing?

14. What is the objection to the use of lead foil for wrapping chewing gum and chocolate?

PROBLEMS

1. How many pounds of tin can be obtained from one ton of cassiterite, if the ore is 95% pure?

2. How many pounds of lead can be extracted from 500 lb. of galena? How many pounds of lead acetate could be made from this lead?

3. How many pounds of copper sulfate can be made from 1000 lb. of cuprous sulfid, Cu_2S ?

4. How many pounds of aluminum are required to reduce the iron in 20 lb. of iron oxid, Fe_2O_3 , by the thermit process?

CHAPTER XL

MANGANESE—CHROMIUM—OTHER ELEMENTS

499. Introductory. Although manganese and chromium do not belong to the same family, they are often treated in the same chapter, since they resemble each other to some extent in chemical properties. Both elements are extracted by heating their oxids with aluminum. Both may act either as *base-forming* elements or *acid-forming* elements. The chief use of both metals is in the manufacture of steels that are very hard and tough. The valence of the elements varies, chromium having a valence of 2, 3, or 6. Manganese may have a valence of 2, 3, 4, 6, or 7.

A. MANGANESE

500. Manganese. The chief ore of this element is *pyrolusite*, MnO_2 . Aluminum is used to reduce this oxid to metallic manganese. The metal itself resembles iron to some extent, but it has a reddish tint. It tarnishes in moist air, and it is readily attacked by the ordinary acids. Its chief use is in making spiegeleisen and ferromanganese. We already know that it finds use in making a very hard steel.

501. Manganese Dioxid. We are familiar with this black oxid of manganese from our experiment on the preparation of oxygen. There it was used as a catalyst. In the manufacture of chlorin, as a "drier" in the paint industry, and in making dry cells, manganese dioxid is an oxidizing agent. In the dry cell an accumulation of hydrogen on the positive plate causes a defect known as polarization. The addition of manganese dioxid serves as a depolarizer. In the manufac-

ture of chlorin by the use of manganese dioxid there is an interesting change of valence:



If any MnCl_4 is formed it immediately breaks down forming chlorin and *manganous* chlorid, MnCl_2 . The valence changes from 4 to 2. When manganese acts as a base former, it generally has a valence of two or three. *Manganous* salts are the more common. They are generally pink in color.

502. Acid-forming Manganese. By the use of certain oxidizing agents on certain manganese compounds it is possible to produce *manganates* and *permanganates*. In these compounds the valence of manganese is 6 and 7 respectively; it acts as an acid-forming element in both cases. The *manganates* are quite unstable.

Potassium permanganate is the most important compound of acid-forming manganese. It is such a vigorous oxidizing agent that its concentrated solution can not be filtered through paper. It forms purplish-red solutions that are decolorized by reducing agents. It is extensively used in analytical work, especially in iron and steel analysis. In an acid solution it gives up its oxygen to a reducing agent as shown by the following equation:



Potassium permanganate finds some use as a disinfectant and antiseptic. It is coming into favor as a bleaching agent.

B. CHROMIUM

503. Chromium. This element is found in nature as *chromite*, FeCr_2O_4 . Chromium is extracted by reduction with aluminum. It is a hard gray metal that does not tarnish in air. The chief use of the metal is in the manufacture of chromium alloy steels. Like manganese, it also acts as a base-former and an acid-former.

504. Base-forming Chromium. As a base-forming element, chromium may form *chromous salts*, in which its valence is 2, or it may form *chromic salts*, in which it has a valence of 3. The latter salts are analogous to the salts of ferric iron. They are green or violet in color and find use as pigments. Since they hydrolyze readily they form good mordants. *Chrome alum*, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, which is also used as a mordant, is formed by evaporating mixed solutions of potassium and chromium sulfates. *Chromic oxid*, Cr_2O_3 , is a green powder which finds use as a pigment under the name of "chrome green."

505. Acid-forming Chromium. *Chromic anhydrid*, CrO_3 , is a red crystalline solid that dissolves in water forming *chromic acid*, H_2CrO_4 . This acid is a very vigorous oxidizing agent. Several of its salts are important compounds. *Lead chromate*, PbCrO_4 , *barium chromate*, BaCrO_4 , and *zinc chromate*, ZnCrO_4 , are all used as yellow pigments. The latter is especially valuable in preventing the corrosion of iron. For that reason structural steel is often painted with this pigment as a first coat. *Potassium chromate*, K_2CrO_4 , is a yellow crystalline solid that finds use in the laboratory.

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, and *sodium dichromate*, $\text{Na}_2\text{Cr}_2\text{O}_7$, are orange-red crystalline compounds. It will be observed that chromium has a valence of 6 in both the chromates and dichromates. If we write the formula of potassium dichromate as $\text{K}_2\text{CrO}_4 \cdot \text{CrO}_3$, the relation between the chromates and the dichromates is apparent. The dichromates are excellent oxidizing agents. Potassium dichromate is used in photogravure and half-tone work, since it forms an insoluble compound with gelatin or asphalt when exposed to the light. It is also used in tanning light leathers since it shortens the process from several weeks, or months, to only a few hours. With concentrated sulfuric acid these dichromates form excellent fluids for cleaning laboratory glassware.

506. Leather is made from the skins of various animals. The hair is first removed by the use of lime. Next the skin is treated with a dilute acid to neutralize the lime and to cause the skin to swell, the process being known as plumping. Tanning changes the skin into leather so that it becomes impervious and does not putrefy. Tan bark from hemlock and other woods produces this change slowly and is the substance used for heavy leathers. Potassium dichromate produces the same change in the presence of a reducing agent by precipitating chromic hydroxid, $\text{Cr}(\text{OH})_3$, in the leather. The leather is then worked with oil to make it soft and less porous. Formaldehyd is used in the tanning of light leathers to make a soft, washable product.

C. OTHER ELEMENTS

507. Introductory. There are several elements which have one or two important applications. On the whole, they may not have sufficient importance to merit discussion in a separate chapter. A number of such elements will be described briefly.

508. Platinum. Platinum occurs native, the Ural Mountains producing the bulk of the world's supply. It is a soft, white metal. Its specific weight is 21.4, it being one of the heaviest metals known. It is very ductile and malleable.

Platinum is not affected by air, nor does it oxidize when heated. It has a high melting point, about 1780°C . No single acid affects it, but aqua regia acts upon it slowly. Fused alkalis attack it quite readily. It forms alloys with several metals. For this reason salts of easily reducible metals like silver and lead should not be heated in platinum ware.

509. Uses. Since platinum is not easily melted and few chemicals attack it readily, it is used for making such laboratory utensils as crucibles, dishes, forceps, etc. Platinum wire and foil find use in all chemical laboratories.

As a catalytic agent platinum is important, especially in the manufacture of sulfuric acid. Platinum is also used in jewelry. Its salts are used in photography. The demand for this metal exceeds the supply and the price is constantly increasing. *Chlorplatinic acid*, H_2PtCl_6 , is the most important compound of platinum.

510. Iridium is a metal that resembles platinum to considerable extent. An alloy containing 90% platinum and 10% iridium is used for making standard weights and measures. It is hard and does not tarnish. Gold pens are alloyed with iridium to increase their hardness.

511. Tungsten is a heavy, silver-white metal that has a very high melting point. We have already learned that large quantities of tungsten find use in making self-tempering steels. Tungsten wire is drawn through diamond dies. Since they can be heated to about 3000°C . without melting, these wires are suitable for making incandescent lamps. Over 90% of the lamps of this type now have tungsten filaments. Tungsten also finds use in making electrical contact points, in X-ray bulbs, and in electric resistance furnaces. *Sodium tungstate* is used for fireproofing cloth.

512. Molybdenum is another metal with a very high melting point. It finds use in making electric furnaces used by dentists. The chief demand for this metal is in the manufacture of special alloy steels for high-speed work.

513. Vanadium is a metal that is used to purify steel. It makes a strong flexible steel. One of its ammonium compounds finds use in making aniline black and in producing a permanent black ink.

514. Titanium serves as a purge in the manufacture of steel. It combines with both oxygen and nitrogen at the ordinary temperature. When titanium is added to the carbon used for making electric arcs it increases the brilliancy of the light. Titanium tetrachlorid was used for making "smoke screens" during the World War.

515. Selenium is an element belonging to the sulfur group. It has one very remarkable property. It is a non-conductor of electricity in the dark, but it becomes a fair conductor when exposed to the light. This property makes it useful in several automatic electrical devices, such as fire alarms and burglar alarms. A method of transmitting photographs by electricity based upon the varying resistance of selenium when exposed to lights of different intensities has been developed.

516. Thorium and Cerium are both extracted from monazite sands. The oxids of these elements glow with a very brilliant light when heated to incandescence. For that reason they are used in making Welsbach mantles. The mantle is woven of ramie or artificial silk and dipped into a solution containing the *nitrates of cerium and thorium* in the proportion of 1% of the former to 99% of the latter. Then the mantle is ignited to convert the nitrates into oxids and dipped into a solution of collodion. The collodion film prevents breakage during shipment, as the oxids are very fragile. An alloy of cerium with iron is used for making gas-lighters, since such an alloy gives off bright sparks when rubbed on a hard file.

SUMMARY

Manganese and chromium are used in making special steels.

Manganese dioxid is an oxidizing agent; it is used in the glass industry and in making chlorin.

Manganese acts as a base-forming element forming chlorids, sulfates, and nitrates. It also acts as an acid-forming element in the manganates and permanganates. *Potassium permanganate* is a crystalline solid used as an antiseptic, a disinfectant, and a bleaching agent.

As a base-forming element chromium forms *chromous* and *chromic* salts. It acts as an acid-forming element in the *chromates* and *dichromates*. *Potassium dichromate* is used in making leather; it is also used in photogravure and half-tone work. Chromium compounds are also used as pigments and mordants.

QUESTIONS

1. What purpose does spiegeleisen serve in making steel?
2. Would the change of a chromate to a dichromate be oxidation, reduction, or neither?
3. Name as many oxidizing agents as you can.
4. Name as many reducing agents as you can that we have studied.
5. Make a list of elements and compounds that we have had which have been used as catalysts.
6. Make a list of compounds we have studied that find use as mordants.
7. How does manganese dioxid serve as a depolarizer in a voltaic cell?
8. Summarize the properties of platinum that make it suitable for use in making laboratory utensils.
9. For what purposes is a silver crucible superior to one of platinum?
10. Why does platinum occur chiefly in the uncombined state in nature?
11. In what ways may tungsten be substituted for platinum?
12. Name three active metals; three inactive metals.
13. Make a list of metals that do not tarnish in air; of metals that are self-protective; of metals that corrode completely.
14. Name two metals that have a low melting point; three metals that melt at a very high temperature.
15. How should the following substances be stored? 1. Sodium; 2. Hydrofluoric acid; 3. White phosphorus; 4. Gasoline; 5. Quicklime.

CHAPTER XLI

RADIUM AND RADIO-ACTIVITY

517. Radio-activity. In 1896 Henri Becquerel, a Frenchman, performed an epoch-making experiment with uranium, an element that finds some use in coloring glass a greenish-yellow. He found that this metal darkens a photographic plate, even when the plate is wrapped in an opaque paper and kept in the dark. It gives off radiations similar to the X-ray. They pass through substances opaque to ordinary light, but they are stopped by metals, bones, etc. Substances like uranium that give off radiations of this nature are said to be *radio-active*.

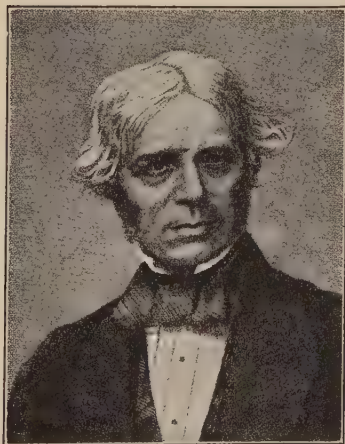
518. Discovery of Radium. Soon after this discovery of Becquerel, M. and Mme. Curie began a series of investigations to determine whether other elements show radio-activity. Thorium was found to be active and Mme. Curie also discovered that pitchblende, the mineral from which uranium is obtained, is several times as active as uranium itself. She concluded that this mineral must therefore contain some other element far more active than uranium. She patiently worked over several tons of pitchblende and succeeded in extracting a few milligrams of the chlorid of an element more than 1,000,000 times as active as uranium. She named this element radium. Radium is usually used in the form of its chlorid, bromid, or carbonate. Mme. Curie succeeded, several years later, in 1910, in isolating metallic radium.

In 1921 Madame Curie, who is now professor of physics at the University of Paris, visited America. The sum of \$120,000 had been raised by subscription among the women



Marie Skłodowska Curie (1867——) was born in Poland. After Henri Becquerel discovered the radio-activity of uranium, Mme. Curie in collaboration with her husband, Pierre Curie, examined other substances in an effort to learn whether they are radio-active. From pitch-blende she isolated radium. She also discovered polonium, another very active element. In 1903 M. and Mme. Curie shared the Nobel prize with Becquerel. She is now professor of physics at the Sorbonne.

Michael Faraday (1791-1867) was a very distinguished English physicist and chemist. While apprenticed to a book-binder he heard Sir Humphrey Davy lecture and wrote him, expressing a desire to be employed in some intellectual pursuit. He studied under Sir Humphrey Davy. He believed that gases are liquids with a low boiling point, and succeeded in liquefying several of them. In chemistry he discovered benzol. In physics he is known for his laws of electrolysis and his studies in electro-magnetic induction leading to the dynamo.



of the United States for the purchase of one gram of radium bromid. This gift of the American women was presented to Madame Curie by the President of the United States.



(Courtesy of Radium Limited U. S. A.)

FIG. 226.—Radiographs. The cut at the left was made by the action of radium rays. The one at the right by the X-rays.

519. Radium. In many respects radium is the most interesting element ever discovered. Its properties are unusual and it *does* things. (1) It affects a photographic plate, even through opaque substances like paper, wood, and very thin sheets of metal. See Fig. 226. (2) Radium and its compounds discharge an electroscope; they knock to pieces the surrounding air molecules, breaking them up into ions and thus making them conductors. See Fig. 227. An electroscope of this type is used to measure the activity of radium salts. Radium is never used as a metal, but it is sold in the form of the bromid or the chlorid, white

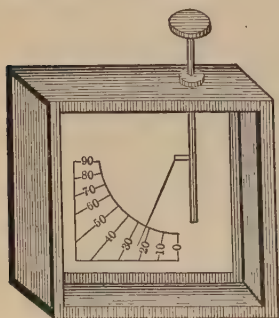


FIG. 227.—An electroscope.

crystalline salts resembling the compounds of barium. In the laboratory we weigh to 0.0001 or possibly to 0.00001 gm., but the electroscope is many times as sensitive for determining the value of radium salts. (3) Radium produces fluorescence with certain substances; when radium salts are mixed with zinc sulfid, a mixture is formed that is luminous in the dark. Such a mixture is used as a luminous paint for coating the dials of air-plane instruments, the hands and dials of watches, and the sights of guns that are to be used for night firing. See Fig. 228. (4) Radium is active chemically; it decomposes water, changes oxygen to ozone, imparts a purple color to glass, etc. (5) Radium produces physiological effects; it produces frightful burns that require a long time to heal. Many early investigators were severely burned by radium while experimenting with it. Radium destroys the germinating power of seeds, destroys bacteria, and kills some small animals. (6) Radium glows in the dark, producing a pale phosphorescence. It does not give light enough to be observed in ordinary daylight. (7) Radium gives off enough heat every hour to melt 1.5 times its own weight of ice; this heat is given off almost continuously, since radium loses only one-half its energy in 1700 years, one-half of what remains in the next 1700 years, and so on.

520. Nature of the Becquerel Rays. The rays emitted by such elements as radium, thorium, and uranium, known as Becquerel rays, have been carefully studied. In 1899 Ernest Rutherford, then of McGill University, discovered that the Becquerel rays are complex, consisting of three different classes:

(1) The α -rays, or *alpha rays*, are identical with *positively* charged helium atoms. Their mass is nearly four times that

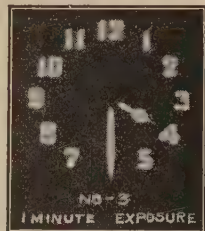


FIG. 228.—Hands of a watch photographed by their radium coating.

of the hydrogen atom; their velocity is from 10,000 to 20,000 miles per second. The alpha rays do not have as great penetrating power as the other rays; a very thin piece of aluminum foil or a thin sheet of paper is sufficient to intercept them. On the other hand, they are very efficient in ionizing air molecules; hence they discharge an electroscope rapidly. Severe radium burns are largely due to the alpha rays.

(2) The β -rays, or *beta rays*, are identical with the electron. They consist of negatively charged particles about $1/1800$ as heavy as the hydrogen atom. Since they travel at a velocity of from 60,000 to 160,000 miles per second, their penetrating power is greater than that of the alpha particles. The *beta ray* seems to be identical with the electrical charge on the negative ion in solution.

(3) The γ -rays, or *gamma rays*, appear to have the same nature as X-rays. They are more penetrating than either the alpha or beta rays. The gamma rays are believed to be caused by the impact of beta particles upon the surrounding matter. Fig. 229 shows the effect of a powerful magnetic field on the complex Becquerel rays emitted from a small particle of radium. The heavy alpha particles are deflected slightly in one direction; the lighter beta particles are deflected more markedly in the other direction; the gamma rays are not deflected at all. By

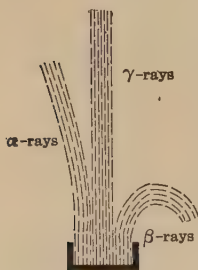


FIG. 229.—Effect of magnet on rays.

the use of such a magnetic field Rutherford studied the radiations from radium and learned their nature.

521. Supply of Radium and Its Uses. *Pitchblende* is one of the sources of uranium, but it is also obtained from *carnotite*, an ore found in Utah and Colorado. *Radium is always found in uranium ores.* In fact it is now known that *uranium is the parent of radium.* But in the radium ores there is only about 1 part of radium to a little more than

3,000,000 parts of uranium. To produce 1 gram of radium about 500 tons of the ore must be used. Fig. 230 shows the large evaporating dishes used to carry out the 75 successive crystallizations needed to separate radium salts from those of barium. The price is generally about \$100,000 per gram. At present (1925) it is a little lower than that



FIG. 230.—Separating radium bromid from barium salts by fractional crystallization.

(\$70,000 per gm.), on account of the discovery of new ore deposits in the Belgian Congo.

We have seen that radium compounds can be used as a luminous paint. See Fig. 231. Since radium compounds destroy bacteria, many attempts have been made to use it in the treatment of certain diseases. The Memorial Hospital in New York has 4 grams of radium from which the emanation is collected in small glass tubes, which are used for

treating cancerous growths. Fig. 232. Physicians are not agreed concerning the value of radium for treating such diseases. In some cases it appears to have been successful, while it has failed miserably in others.

522. Disintegration of the Atom. Because radium and its compounds appear to give off heat and light indefinitely, it was at first believed that they do not conform to the law of the conservation of energy. Then more careful investiga-



FIG. 231.—Girls at work coating small objects with paint that contains a trace of radium.

tions were made and it was discovered that radium compounds do lose their energy slowly.

Then the question arose, "What is the source of all this energy that is liberated?" A long series of experiments has furnished the answer to this question. *The atoms of radium and other radio-active substances are exploding or disintegrating.* The alpha and beta rays that we have just studied are products of atomic disintegration. Spontaneously certain heavy atoms are breaking down into simpler and lighter atoms. Uranium has an atomic weight of 235; it is the heaviest atom known. The atomic weight of radium is 226. If a

little radium is placed in a sealed tube and let stand for some time, two gases will be formed. When the tube is examined, it is found to contain *helium* and *niton*. The latter gas has an atomic weight of 222; it is commonly called *radium emanation*. Thus we see that as the radium atom explodes, it forms

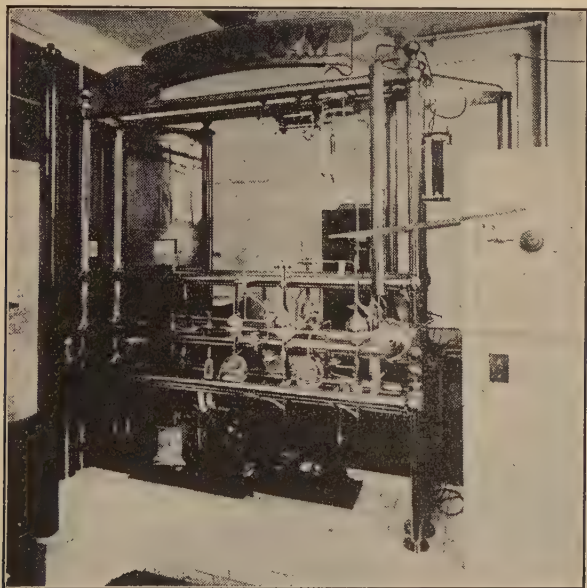


FIG. 232.—Apparatus for collecting radium emanation from radium.

niton and helium. The heat is evidently due to collisions between the particles emitted as the explosion occurs. The average life of a radium atom is about 2500 years. Since radium loses half its activity in the first 1700 years, and one-half of what remains in the next 1700 years, its period of half-decay is said to be 1700 years. The niton which is formed from radium also disintegrates, forming *Radium A*, an element having an atomic weight of 218. Helium is also

formed. *Radium emanation* has a period of about 5 days. *Radium A* breaks up into *Radium B*, which in turn disintegrates to form successively *Radium C*, *D*, *E*, and *F*. *Radium F* has an atomic weight of 206. It is an *isotope* of lead. The old alchemists believed that it was possible to *transmute* one element into another. Chemists have scoffed at such ideas of transmutation, only to learn that at least three elements undergo *spontaneous transmutation*.

523. Can Atomic Energy be Utilized? We have learned that one gram of good coal in burning yields about 8000 calories. It is possible to compute the amount of heat liberated by one gram of radium when disintegrating, since we know that one gram yields about 120 calories of heat per hour throughout an average life of about 2500 years. The total amount is more than 300,000 times as much heat as can be obtained by burning an equal weight of coal.

J. J. Thomson has estimated that the energy stored in one gram of *hydrogen* equals 6×10^{11} foot pounds. This energy given off by one gram ($1/454$ lb.) of hydrogen would be sufficient to lift 10 of our largest battleships (32,000 tons each) to the top of Mt. Blanc, over $3\frac{1}{2}$ miles. Whether man will ever learn how to unlock this tremendous storehouse of energy and put it to practical use is problematical. There is no known chemical or physical agency that either accelerates or retards the disintegration of atoms.

It is reported that Rutherford succeeded recently in disintegrating the nitrogen atom by the action of radio-active substances themselves. This appears to be a step toward solving this interesting problem, but we must consider that Rutherford used as much energy to knock the nitrogen atoms to pieces as he obtained from the disintegration. Therefore the biggest part of the problem remains to be solved. Possibly at some future time atomic energy may be used to replace coal and gasoline for fuel and power purposes. It is also

possible that future generations may learn how to transmute lead and other base metals into more precious ones. No one can foretell what the future may bring, especially when we consider the rapid strides that physics and chemistry have made during the last few decades.

CHAPTER XLII

CHEMISTRY OF THE COMPOUNDS OF CARBON

A. SOURCES

524. Introductory. The compounds formed by plants and animals were formerly included in *organic chemistry*, since it was believed that some living organism was needed to produce them. This name is still used for such compounds, elementary carbon and the carbonates usually being included with inorganic substances. In 1828 Wohler, a German chemist, prepared urea by synthesis. Since that date a large number of the compounds formerly obtained from plants and animals have been made in the laboratory. Since all these compounds contain carbon, "the chemistry of the compounds of carbon" seems to be a more fitting name for this division of chemistry.

525. Source of Carbon Compounds. We have already learned that certain hydrocarbons and some other carbon

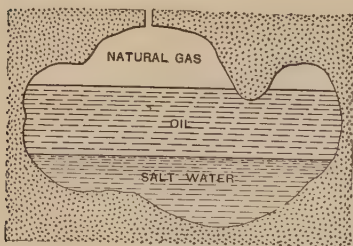


FIG. 233.—Possible condition of an underground oil reservoir.

compounds are obtained by the destructive distillation of wood and soft coal. Many hydrocarbons are obtained from petroleum and coal tar. Alcohol is obtained by the fermentation of fruits and grains. The fruits also yield organic acids and sugar. Starch is made from the cereals, while fats and oils

are obtained from animals, nuts, and seeds. Cellulose comes from cotton and various other vegetable fibers.

526. Petroleum. Petroleum is a thick liquid, often of a greenish-black color, that is obtained from the earth's crust. It may be found near the surface or at a depth of 2000 or more feet. Holes about 6 to 8 in. in diameter are drilled in the earth until the oil stream or reservoir is reached. See Fig. 233. If considerable natural gas is present, the oil is



FIG. 234.—A gusher.

forced out forming what is called a “gusher.” See Fig. 234. Some wells of this kind flow several hundred barrels of oil per day. The oil may rise to a point near the surface from which it is pumped into storage tanks. The *crude oil* is then pumped through pipe lines to the refineries, sometimes for a distance of 1500 miles. See Fig. 235.

527. Refining Petroleum. Petroleum is a mixture of several hydrocarbons, of which petroleum ether, gasoline,

naphtha, benzine, kerosene, gas oils, lubricating oils, vaseline, and paraffin are the most important. They may be separated from one another by *fractional distillation*. Fig. 236 shows the method of separating petroleum into several distillates by fractional distillation. From these distillates many products are obtained by further fractionation. In purifying these oils they are washed with sulfuric acid, an alkali, and water in turn. At one time kerosene was a more valuable

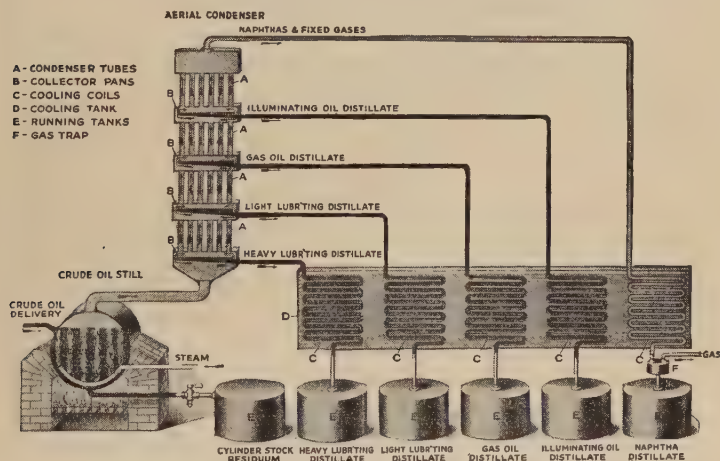


FIG. 235.—General view of oil field, showing derricks and temporary storage tanks.

product than gasoline. Now the gas engine in the automobile has changed conditions and the refiners of petroleum are trying to increase the yield of gasoline. By reference to the table on page 507, the student will observe that a hydrocarbon becomes less volatile as its molecule becomes heavier. For example, $C_{10}H_{22}$ boils at $173^{\circ} C.$, while hexane, C_6H_{14} , boils at $71^{\circ} C.$ The first is difficult to vaporize and one would find it difficult to start a gasoline engine on such a fuel. If, however, the molecule can be split into two or more parts,

the amount of volatile fluid is increased. That is exactly what is done in the so-called "cracking" process. The heavy molecules are broken up to increase the amount of volatile matter. To accomplish this the oils are superheated.

528. Uses of Petroleum Products. *Petroleum ether* is used as a solvent. *Gasoline*, *naphtha*, and *benzine* are used as solvents; they are also extensively used as fuels, especially



(Courtesy of Platt & Washburn Refining Company.)

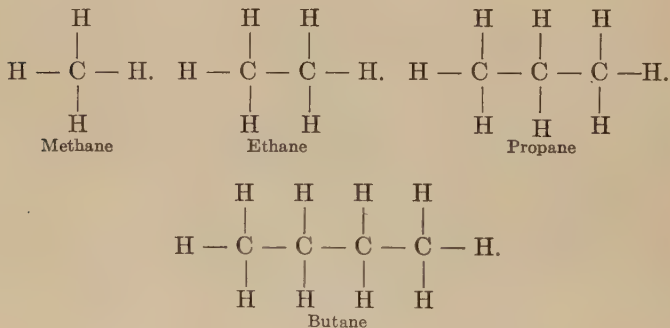
FIG. 236.—Fractional distillation of crude petroleum.

in internal-combustion engines. Benzine is sometimes used as a substitute for turpentine. *Kerosene* serves as a fuel and is used for illuminating purposes. It should have a flash-point of at least 110° F. to make it safe for use in lamps. *Vaseline* serves as an ointment and as a lubricant for use as cup-grease and axle-grease. *Paraffin* is used in making candles and chewing gum; it also finds use for insulating electrical apparatus and in waterproofing paper and fabrics. Those portions of petroleum which are not of value for lubrication are used as a fuel. Many of our battleships are

oil burners. *Fuel oil* is also used for heating homes and public buildings.

B. HYDROCARBONS

529. Hydrocarbons. A *hydrocarbon* is a compound of *hydrogen* and *carbon*. Since the valence of carbon is 4, we might expect that CH_4 would be the only compound of these two elements. As a matter of fact more than 200 hydrocarbons are known. Such a large number is possible since one carbon atom has the rather unusual ability of combining with other carbon atoms, as the following structural formulas show:



If we examine these formulas we will observe that each one differs from the preceding one by the group, CH_2 . A series of compounds each differing from the preceding by such a group, or *homolog*, is known as an *homologous series*. The homolog, CH_2 , is very common in organic chemistry. These compounds form the first four of the *paraffin series*, or the *methane series*. The following table gives a few of the 60 known representatives of this series:

Name	Common name	Formula	Melting point	Boiling point
Methane.....	Marsh gas.....	CH ₄		Gases { - 164° C. - 90° C. - 37° C. 1° C. 36° C.
Ethane.....		C ₂ H ₆		
Propane.....		C ₃ H ₈		
Butane.....		C ₄ H ₁₀		
Pentane.....	A mixture of pentane and hexane forms <i>petroleum ether</i>	C ₅ H ₁₂		
Hexane.....	A mixture of hexane and heptane forms <i>gasoline</i>	C ₆ H ₁₄		Liquids { 71° C. 98° C. 125° C. 150° C. 173° C.
Heptane.....	A mixture of heptane and octane forms <i>naphtha</i>	C ₇ H ₁₆		
Octane.....	A mixture of octane and nonane forms <i>benzine</i>	C ₈ H ₁₈		
Nonane.....		C ₉ H ₂₀		
Decane.....	A mixture of hydrocarbons from decane to hexadecane is <i>kerosene</i>	C ₁₀ H ₂₂		
Hexadecane.....		C ₁₆ H ₃₄	18° C.	Solids { 288° C.
Hexacontane.....		C ₆₀ H ₁₂₂	102° C.	

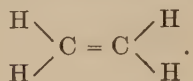
A study of the above table shows that the melting points and the boiling points of these hydrocarbons rise as the molecular weight increases. It is not necessary to memorize the formulas since the number of hydrogen atoms in the compound can be obtained by multiplying the number of carbon atoms by two and adding two to the product. Thus the general formula for hydrocarbons of this series is C_nH_{2n+2} .

530. Methane. CH₄. This gas is formed in nature by a decomposition of organic compounds. It forms about 90% of *natural gas*. It is liberated when the mud at the bottom of stagnant pools of water is stirred, hence the name *marsh gas*. It is frequently found in coal mines and called by the miners *fire damp*. It may be made in the laboratory by the action of aluminum carbide on water:

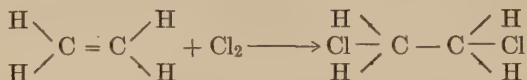


Methane burns with a pale yellow flame. It is used as a fuel.

531. Ethylene, C_2H_4 , is the first member of a *second* series of hydrocarbons. Its structural formula is



An organic compound having a *double* bond between two carbon atoms is said to be *unsaturated*, since other elements may be added to it directly to form new compounds. For example, two chlorine atoms may be added directly to ethylene as shown by the following equation:



Ethylene gas burns with a bright flame. It finds use as an illuminant. During the war, enormous quantities of ethylene were made to be used in the manufacture of *mustard gas*. While there are many other hydrocarbons in this series, yet we can not discuss them all in an elementary text-book. In the acetylene series, we shall refer to only one compound.

532. Acetylene, C_2H_2 , has already been studied as to preparation, properties, and uses. It is even more unsaturated than ethylene, since it has a triple bond between its carbon atoms. Its structural formula, $H - C \equiv C - H$, indicates that either two or four univalent elements can be added directly. Such is the case. Let us next study a hydrocarbon in the *aromatic* series.

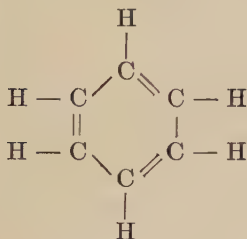
533. Benzol, C_6H_6 . *Benzol*, or *benzene*, is a *polymer* of acetylene, having the same percentage composition, but a different formula and a higher molecular weight. It can be prepared when acetylene is passed through a hot tube:



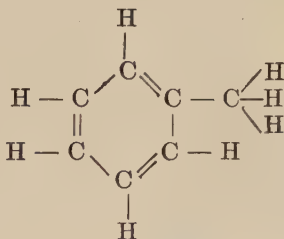
Thus it seems to be formed by "bunching" acetylene molecules. *Commercially* benzol is obtained from the distillation

of coal-tar. Those who work with benzol should be very careful not to inhale its vapor, since it produces anemia. Three hydrocarbons in this series are quite well known: *Benzol*, C_6H_6 , is the simplest; *toluol*, C_7H_8 , we found was used for making T. N. T.; *xylol*, C_8H_{10} , is also a coal-tar product.

All of these compounds find extensive use in the manufacture of dyestuffs. They are good solvents; toluol also finds use in making explosives. The following structural formulas are generally accepted as being the correct formulas for benzol and toluol:



Benzol, or benzene



Toluol, or toluene

534. Other Hydrocarbons. *Naphthalene*, $C_{10}H_8$, is a coal-tar compound. It crystallizes in white shining scales. It is used in "moth-balls" and in the manufacture of drugs and dyestuffs. *Anthracene*, $C_{14}H_{10}$, is also obtained from coal tar. It is used in the preparation of alizarin, a red dye. *Turpentine*, $C_{10}H_{16}$, is a hydrocarbon obtained from the long-leaved pine. It is used medicinally and also in the paint and varnish industry. *Asphalt* consists chiefly of a natural mixture of hydrocarbons. The island of Trinidad furnishes large quantities of asphalt, which is used for paving streets.

C. SUBSTITUTION PRODUCTS OF THE HYDROCARBONS

535. Preparation. Substitution products of the hydrocarbons are prepared by replacing one or more of their

hydrogen atoms with elements like the halogens, or with such groups as OH, NO₂, etc. For example, *mono-chlor-methane*, CH₃Cl, may be made by treating methane with chlorin:



By further treatment with chlorin, other hydrogen atoms are replaced in turn, resulting in the formation of such compounds as CH₂Cl₂, CHCl₃, and CCl₄. Ethane and other hydrocarbons form substitution products. The radical

C₂H₅ is called "ethyl." *Tetra-ethyl lead* is used with gasoline to prevent "motor knocks."



FIG. 237.—Pyrene extinguisher.

536. Chloroform. CHCl₃. Although chloroform is a substitution product of methane and could be made by the action of chlorin on this gas, yet it is cheaper and far more convenient to make it by the action of chlorin on alcohol when an alkali is present. Chloroform is a heavy, oily liquid. It has a sweet, rather pleasing odor. Its vapor produces insensibility to pain when inhaled, hence chloroform is used as an anesthetic. It finds some use as a solvent.

537. Iodoform. CHI₃. Like chloroform, iodoform is also made from alcohol. It is a yellow crystalline solid, having a very persistent odor. It is used chiefly as an antiseptic-surgical dressing.

538. Carbon Tetrachlorid. CCl₄. This compound is a colorless compound somewhat resembling chloroform. It is used extensively as a solvent. For removing grease spots and other stains it is quite as good as gasoline, and its vapor is not explosive. "Carbona," a cleansing fluid, contains carbon tetrachlorid.

It is also used in some small fire extinguishers, for example, "Pyrene." Fig. 237 shows a sectional diagram of the "Pyrene" fire extinguisher.

539. Nitrobenzol. $C_6H_5NO_2$. If benzol is treated with nitric acid in the presence of sulfuric, a heavy oily liquid known as nitrobenzol is formed, the NO_2 group being substituted for one of the hydrogen atoms of the benzol. It is used extensively in the manufacture of aniline.

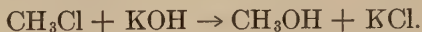
540. Aniline. $C_6H_5NH_2$. Aniline formerly came from the anil plant but it is now generally made by treating nitrobenzol with nascent hydrogen. Enormous quantities are used in the dye industry. *Toluidine* and *xylidine*, compounds made from toluol and xylol respectively in a manner analogous to the making of aniline, are also used in the dye industry. When we stop to consider that benzol, toluol, xylol, naphthalene, and anthracene are all coal-tar compounds, we can readily understand why this tarry mixture is so important in the *dye industry*.

D. ALCOHOLS

541. Alcohols. The alcohols all have one or more OH groups. Although they can be formed indirectly from the hydrocarbons, they are more often prepared by other methods. For example, wood alcohol is made by the dry distillation of wood; it is called *methyl alcohol* since it differs from methane only in the fact that an OH group has been substituted for one of the hydrogen atoms of that gas. To prevent people from mistaking wood alcohol for grain alcohol and being fatally poisoned wood alcohol is now called *methanol*. Grain alcohol is made by the fermentation of fruits and grains. A large number of alcohols are known to the organic chemist, but these two are the most important ones.

542. Wood Alcohol. CH_3OH . In this alcohol the group CH_3 acts like a radical. It is called *methyl*. If we treat

methyl chlorid with potassium hydroxid, wood alcohol is formed:



This method of preparing wood alcohol would be more costly than the commercial method from the destructive distillation of wood.

Pure wood alcohol has rather a pleasant odor, but the commercial product contains impurities that impart to it a disagreeable odor. It is a light liquid, boiling at 66.7°C . It is very poisonous; cases of poisoning from wood alcohol even when used externally are not uncommon. Its vapor attacks the eyes. When taken internally or inhaled, it often affects the optic nerve, producing partial or total blindness. It is a good fuel, since it burns with a hot smokeless flame. It also finds use as a solvent of oils, resins, and shellac.

543. Fermentation. If we add a little yeast to a dilute water solution of sugar or molasses, chemical action soon takes place. Bubbles of gas, which are found to be carbon dioxid, are liberated and alcohol is formed in the solution.



Any chemical change that is brought about by the action of some organic body, or ferment, is known as fermentation. The organic body in the above example is an *enzyme* secreted by the yeast plants. The enzyme acts like a catalytic agent in changing the sugar into alcohol and carbon dioxid. This type of fermentation, in which alcohol is formed, is known as *vinous fermentation*. There are many types of fermentation, certain kinds of bacteria being active in producing the chemical change. Thus the making of vinegar, the souring of milk, the formation of rancid butter, and the decay of foods are all examples of fermentation caused by plant organisms.

544. Grain Alcohol. $\text{C}_2\text{H}_5\text{OH}$. We have seen that ordinary alcohol can be produced by the action of an enzyme

on fruit juices or dilute sugar solutions. On a large scale it is prepared by the fermentation of such starchy grains as barley, rye, and corn. These grains are first sprouted to change the starch to sugar, this change being produced by the ferment *diastase*. They are then crushed and treated with water and yeast to produce alcoholic fermentation.

Beer, claret, ale, hard cider, and the various *wines* are all beverages that are produced by fermentation of fruits or grains. They are known as *fermented liquors*. When the per cent of alcohol in a fermented liquor amounts to about 14%, fermentation stops, since alcohol of this strength renders the ferment inactive. Stronger liquors are made by distillation or by *fortifying* fermented liquors by the addition of alcohol.

In producing a *distilled liquor* some fermented liquor, which we have seen contains not more than 14% of alcohol, is heated until the boiling point of alcohol (78° C.) is reached. The mixture is boiled until all the alcohol is driven off, but the distillate that condenses contains some water, as water evaporates quite rapidly at 78° C. The per cent of alcohol is, however, much higher than that of the original mixture. By re-distilling this distillate, the per cent of alcohol is increased still more. *Whisky, brandy, gin, and rum* are distilled liquors containing from 50 to 80% alcohol.

A liquid containing more than 95.5% alcohol can not be obtained by fractional distillation, since a mixture containing 95.5% alcohol and 4.5% water boils at a slightly lower temperature than pure alcohol, and distils as a uniform mixture. *Ordinary alcohol* is 95% alcohol. The last traces of water may be removed from alcohol by adding to it some dehydrating agent; generally lime is used. *Absolute alcohol* is water free, or nearly 100% pure.

Since grain alcohol is really a substitution product of ethane, its chemical name is *ethyl alcohol*. It is sometimes known as *ethanol*. Alcohol is a colorless liquid, having a peculiar odor and a sharp, biting taste. It has a strong

affinity for water and mixes with it in all proportions. It is not so poisonous as wood alcohol, but when taken internally it produces intoxication. During the first stages, it causes the blood to flow to the surface, thus producing a feeling of warmth and vigor that has led to the popular idea that alcohol is a stimulant. Later the heart action becomes slower and the temperature falls below normal, showing that alcohol is really a *narcotic*. Alcohol burns with a nearly colorless blue flame.

In addition to the use of alcohol as a beverage, it finds some use as a fuel. It is an excellent solvent of resins and is used in the varnish industry. In pharmacy it is used for extracting from plants their medicinal constituents. Thus such substances as bay rum and witchhazel extract contain from 15 to 20% alcohol. *Tincture of iodine* contains 7% of iodine dissolved in alcohol. Lemon extract should contain not less than 5% lemon oil. To dissolve this oil alcohol of about 80% strength is needed. Vanilla extract is made from resins of the vanilla bean dissolved in 50% alcohol.

545. Denatured Alcohol. Prior to 1907 an internal revenue tax of about \$2.00 per gallon had been levied on all alcohol made in the United States, whether it was to be used for industrial purposes or as a beverage. Since manufacturers in this country who used considerable quantities of alcohol could not compete with foreign manufacturers who had no tax to pay, Congress in 1906 passed a law making alcohol which is to be used for industrial purposes exempt from taxation, provided it is properly "denatured." Grain alcohol is "denatured" by mixing 90 to 95 parts grain alcohol, $4\frac{1}{2}$ to 10 parts of methanol, and $\frac{1}{2}$ part of benzol. The addition of these substances renders it unfit to be used as a beverage, but it does not interfere with its use in the industries and arts. Considerable quantities of "denatured" alcohol are used in the winter time to keep automobile radiators from freezing.

546. Glycerol. $C_3H_5(OH)_3$. *Glycerin*, or *glycerol*, is a triacid alcohol. It is a thick viscid liquid, colorless and odorless, but having a sweet taste. Its most important use is in the manufacture of nitroglycerin. It is also used in some toilet soaps, and medicinally in various lotions.

547. Phenol. C_6H_5OH . Chemically *phenol* is an alcohol obtained from coal tar, but since it has very feeble acid properties it is commonly known as *carbolic acid*. It is closely related to benzol, as its formula indicates. Pure phenol forms colorless crystals, having a peculiar, persistent odor. It is used in making picric acid for explosives and as a disinfectant. It is now being used with formaldehyd to form such substances as bakelite and condensite which are used for insulating materials, phonograph discs, etc.

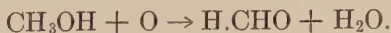
The *cresols* are hydroxids of toluol that find extensive use in preserving wood. They are excellent disinfectants.

E. ETHER

548. Ether. $(C_2H_5)_2O$. Ether is formed by heating alcohol with sulfuric acid at the proper temperature. Ethers are organic oxids. Ordinary ether, or ethyl ether, is a light mobile liquid boiling at about $35^\circ C$. It is used to some extent as a solvent, but more extensively as an anesthetic. Nitrated cellulose forms in ether a colloidal suspension. From the jelly-like mass smokeless powder is formed.

F. ALDEHYDS

549. Formaldehyd. $H.CHO$. Aldehyds are prepared by the partial oxidation of alcohols. *Formaldehyd*, the most important of this group of compounds, is prepared by partially oxidizing wood alcohol:



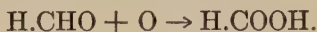
This aldehyd is a gas at temperatures above $21^\circ C$. It is sold under the name *formalin*, which is a 40% water solu-

tion of the gas. It is one of the best disinfectants known. Formalin is often used on seeds before planting to destroy injurious fungi. Potatoes so treated are less apt to be affected by scab. It also finds use in preserving anatomical specimens, and illegally as a food preservative.

Benzaldehyd, $C_6H_5.CHO$, is found in almonds and in cherry kernels. It is used as a flavor. Vanillin, $C_7H_7.CHO$, is an aldehyd extracted from the vanilla bean, or it may be made synthetically. It is used as a flavor in vanilla.

G. ORGANIC ACIDS

550. Acids. If we oxidize the aldehyd studied in the last section, an organic acid is formed:



All organic acids have one or more *carboxyl* ($COOH$) groups. A very large number are known, some of them being quite important compounds. While they can be made by the oxidation of their corresponding alcohol or aldehyd, the majority of them are obtained from their salts found in plants. Some of them are produced by fermentation.

551. Formic Acid. $H.COOH$. This acid stands first in an homologous series of organic acids related to the paraffin series of hydrocarbons. It is found in nature in red ants, in some bee stings, and in stinging nettles. Although a weak acid chemically, yet physiologically it is active enough to blister the skin. Its salts, known as *formates*, are used as mordants.

552. Acetic Acid. $CH_3.COOH$. This acid is obtained by the destructive distillation of wood. It is also formed by the action (on alcohol) of a ferment known as "mother of vinegar." In this manner the alcohol in hard cider is slowly changed to acetic acid:



Acetic acid containing less than 0.5% water crystallizes at a temperature of 16° C. forming *glacial acetic acid*. This acid is a good solvent of organic substances. Its salts known as *acetates* have the $(C_2H_3O_2)$ radical; they are used as mordants.

Acetic acid is the active substance found in vinegar, it being present to the extent of from 4 to 6%. *Natural vinegar* is made by two successive fermentations of the juices of fruits, usually from the juice of apples. *Artificial vinegar* is made by the oxidation of alcohol.

553. Oxalic Acid. $(COOH)_2$. Oxalic acid is a white crystalline solid. Since it has two carboxyl groups, it is a dibasic acid. Its salts, the oxalates, are found in several plants, such as rhubarb, oxalis, and other sorrels. It is an active poison. Oxalic acid finds use in calico printing, as a reducing agent, in bleaching flax and straw, and in cleaning brass and copper.

554. Tartaric Acid. $(CHOH)_2(COOH)_2$. When grape juice ferments, "tartar," or impure acid potassium tartrate, is deposited in the form of crystals, since it is insoluble in alcohol. From this "tartar" the acid may be obtained. Acid potassium tartrate, $HK(C_4H_4O_6)$, is *cream of tartar*. Both the acid and this salt are used in baking powder. Sodium potassium tartrate is known as Rochelle salts.

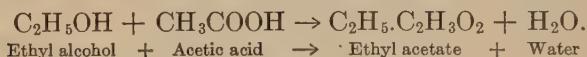
555. Citric Acid. $C_3H_4 \begin{matrix} \diagup OH \\ \diagdown (COOH)_3 \end{matrix}$. This acid is found in lemons and other citrous fruits. It also occurs in raspberries, gooseberries, and currants. Its magnesium salt is used in medicine.

H. ETHEREAL SALTS OR ESTERS

556. Occurrence. Many esters are found in nature in fats and oils, as well as in certain volatile oils that give to plants and their fruits their odor and flavor. Since many of them have a pleasant odor, the name *ethereal salts* is often

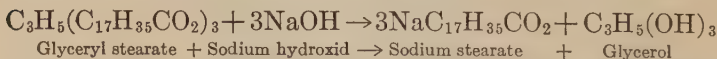
given to this class of compounds. For example, oil of winter-green is a salt of wood alcohol and salicylic acid known as methyl salicylate. Banana oil, which is used in aluminum paint, is amyl acetate. An ethereal salt of ethyl alcohol and butyric acid has the flavor of pineapple extract. This is rather interesting when we consider that butyric acid is present in rancid butter.

557. Preparation of Esters. Esters may be prepared by the action of an alcohol on an organic acid. For example,



The alcohol acts like a base in neutralizing the acid to form an ethereal salt. Since many esters are salts of very weak acids and very weak bases they hydrolyze readily. For this reason the above reaction is reversible unless some dehydrating agent like sulfuric acid is present to take up the water that is formed. Esters are also formed when an alcohol is acted upon by an inorganic acid. Thus we have seen that nitric acid acts upon glycerol to form *glyceryl nitrate*, or *nitroglycerin*, an ethereal salt.

558. Saponification. Many of the common fats and oils are glyceryl salts of such organic acids as stearic, palmitic, and oleic. They are ethereal salts, or esters. *Stearin*, the glyceryl salt of stearic acid, forms the chief constituent of beef and mutton tallow. *Palmitin* is a salt of palmitic acid found in palm oil. *Olein* is a salt of oleic acid that forms a considerable proportion of lard, olive oil, and cottonseed oil. When these fats or oils are treated with a strong base like sodium hydroxid, the sodium salt of these acids, or *soap*, is formed and *glycerol* is obtained as a by-product:



Saponification may be defined as the process of converting fats or oils into soap by treating them with a strong base. More

broadly, it includes the hydrolysis of all esters. Soap is usually a mixture of the sodium salts of the organic acids mentioned above. For example, Castile soap is sodium oleate made by boiling a low-grade olive oil with sodium hydroxid. See Fig. 238. *Soft soaps* and *liquid soaps* are

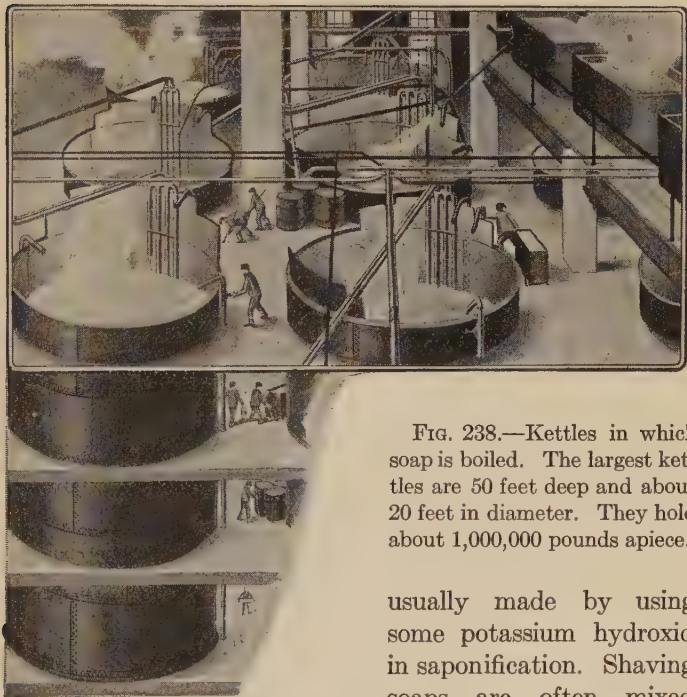


FIG. 238.—Kettles in which soap is boiled. The largest kettles are 50 feet deep and about 20 feet in diameter. They hold about 1,000,000 pounds apiece.

usually made by using some potassium hydroxid in saponification. Shaving soaps are often mixed sodium and potassium salts of the above acids. When soap is added to hard waters the sodium and potassium salts, which are soluble, unite with the calcium and magnesium salts in the hard water to form "lime soap" or "magnesium soap." Both of these compounds are insoluble, and no suds can be produced until enough soap has been added to precipitate them completely. A soap that will

lather in sea-water, known as *marine soap*, is made from cocoanut oil. It contains a high per cent of water.

559. Fillers and Adulterants. In the manufacture of soap some water is incorporated with it. The soap is then dried to give it the proper hardness and prevent its dissolving too rapidly. A hard soap should not contain more than 25% of water. *Rosin* is nearly always added to a laundry soap since it increases its lathering power. As it aids in the cleaning process, rosin should be classed as a filler rather than as an adulterant. *Sodium silicate* is added as a filler in some soaps. Its cleansing properties are slight, and it is injurious to certain fabrics, hence it is sometimes classed as an adulterant. A laundry soap usually contains a slight excess of the base to aid in removing grease or oil from the fabrics. A toilet soap should not contain free alkali as it will cause the skin to chap or crack.

560. Cleaning and Laundering. Dirt may usually be readily removed from the clothing by the mechanical action of water unless grease or oil is present. In such a case the grease sticks to the fiber and the dirt which adheres to it can not be removed since the binding material is insoluble in water. Soap is water-soluble and it owes its cleansing power to its ability to form an emulsion with fats and oils. The minute fat globules which are held in suspension by the soap solution are easily carried away by the agitation of the water.

Wool and silk are usually "dry cleaned," since they are apt to be injured by the action of soap and water. In the "dry cleaning" process some substance like gasoline, benzol, or carbon tetrachlorid, is used to dissolve the grease. It may then be absorbed by the use of blotting paper, or with such powders as French chalk or fuller's earth. Carbon tetrachlorid is one of the safest solvents to use since its vapor does not form explosive mixtures with air.

561. Special Soaps and Scouring Powders. The *floating soaps* are made by beating air into the soap while it is still

liquid. *Transparent soaps* frequently contain glycerin. They may also be made by dissolving the soap in alcohol. Dyes and perfumes are generally added to toilet soaps. The various *medicated soaps* are made by adding to them some substance of supposed medicinal value. *Powdered soaps* are made by grinding a dry, hard soap to a fine powder. If such a soap is to be used in the laundry, sodium carbonate is usually added. *Naphtha soaps* contain a small per cent of naphtha.

Scouring powders are generally mixtures of powdered soap, sodium carbonate, and such gritty substances as powdered sand or pumice stone. Many of them contain from 80 to 90% of insoluble matter.

562. Butter—Oleomargarine. Butter is an animal fat obtained from milk. The federal law requires that butter shall contain at least 82.5% fat and not more than 16% water. These fats are mainly olein, stearin, and palmitin, but the flavor of butter is largely due to an ester of butyric acid and the presence of small quantities of ethereal salts of capric, caproic, and caprylic acids. Certain bacteria cause butter to ferment or become rancid, the disagreeable odor in such event being due to the formation of the acids from the last four esters mentioned. Butyric acid has an unpleasant odor and taste. Capric acid is present in limburger cheese. As these acids are volatile, such butter may be *renovated* by melting the fat and blowing air through the molten fat for several hours. Such butter is also called *process butter*.

Oleomargarine is a butter substitute. It is made from neutral lard, beef fat, cottonseed oil, and palm oil. It is cheaper than butter and is considered just as nutritious. Few persons can tell the difference between butter and oleomargarine by the taste alone. Nut margarine is made from peanut oil and cocoanut oil.

Butterine is made by adding a certain per cent of butter to oleomargarine.

SUMMARY

Organic chemistry is known as the chemistry of the compounds of carbon.

Carbon compounds are obtained by the *destructive distillation* of wood and coal, from the *fractional distillation* of petroleum, and from various plants and animals.

A *hydrocarbon* is a compound containing hydrogen and carbon only. More than 200 are known. They are used extensively as fuels and solvents. Methane, acetylene, benzol, gasoline, kerosene, vaseline, paraffin, naphthalene, and turpentine are all common examples of hydrocarbons.

Certain elements or groups of elements may be substituted for one or more of the hydrogen atoms in a hydrocarbon. Chloroform, iodoform, carbon tetrachlorid, and aniline are important *substitution products* of hydrocarbons.

Fermentation is a chemical change produced by the action of a living organism or an enzyme.

The *alcohols* are organic compounds consisting of an organic radical and at least one OH group. Ordinary alcohol is made by the fermentation of sugar. Methyl alcohol, glycerol, and phenol are also important alcohols.

An *ether* is an oxid of organic radicals. Ethyl ether is the most common, being used as an anesthetic.

Aldehyds have the CHO group. Formaldehyd is the most common aldehyd. It finds use as a disinfectant and preservative.

Organic acids have the carboxyl (COOH) group. Acetic acid occurs in vinegar. Tartaric acid finds use in baking powder.

Esters are salts of alcohols and acids. They include animal and vegetable fats and oils, fruit flavors, perfumes, nitroglycerin, etc. Butter and oleomargarine are mixtures of esters or ethereal salts.

Saponification is the process by which fats and oils are converted into soap by boiling them with a strong base.

QUESTIONS

1. What do you understand by an homologous series? Does the relation appear to hold in the same manner in organic acids?
2. Why is petroleum such an important substance from an industrial standpoint?
3. If you were given a substance containing carbon 92.3 %

and hydrogen 7.7 % how could you tell whether it was acetylene or benzol vapor?

4. What is the advantage of using structural formulas in organic chemistry?

5. At one time coal tar was thrown away as waste material. Why is it so valuable at the present time?

6. Is wood alcohol suitable to use as an alcohol rub? Give reason for your answer.

7. Why is alcohol so important in pharmacy?

8. Name one very important part that sulfuric acid plays in organic chemistry. Illustrate, using at least three different cases.

9. Would it be possible to produce formic acid by starting with methane? If so, name the different steps in the process.

10. Why does baking soda relieve the pain from bee stings?

11. Name some common fillers used in soap. Should they be classed as adulterants?

12. Why does not a mixture of gasoline and water make as good a cleansing solution as soap and water?

13. Castile soap is often mottled by putting into it ferrous sulfate. This produces green spots. Why do they become red when exposed to the air?

14. State the advantages and disadvantages of using a soap that contains free alkali.

CHAPTER XLIII

OTHER CARBON COMPOUNDS

A. CARBOHYDRATES

563. Carbohydrates include the various sugars, starch, cellulose, and dextrin. They all contain carbon, hydrogen, and oxygen. In nearly all cases the hydrogen and oxygen are present in the ratio of 2 to 1, the same as in water.

564. Sugars. Many sugars are known, of which *glucose*, *fructose*, *maltose*, *sucrose*, and *lactose* are the most important. *Cane sugar*, *beet sugar*, and *maple sugar* all contain *sucrose*, $C_{12}H_{22}O_{11}$. Cane sugar is made by squeezing the juice from sugar cane as the stalks are passed between rollers. It is then clarified by precipitation and by filtering it through bone black. To avoid scorching the sugar and to facilitate evaporation, the syrup is concentrated in vacuum pans. See Fig. 239. The student should remember that liquids boil at lower temperatures when the atmospheric pressure is decreased. The "mother liquor" left after the crystals of sugar have been removed is known as *molasses*. Pure sugar crystals have a natural yellow tint; before sugar is put on the market this yellow tint is neutralized by the addition of some blue pigment, usually ultramarine. Beet sugar is made from beets in a similar manner. Maple sugar contains some flavoring material that gives it a different taste from beet sugar and cane sugar, although it consists largely of sucrose.

When sucrose is heated to 210° C. *caramel* is formed. This substance is used as a flavoring in candy and ice cream and as a coloring matter. If we add an acid to sucrose and heat it to about 70° C. the sucrose is converted into two

sugars, *dextrose* and *levulose*. The process is known as *inversion*; *invert sugar* forms a sticky substance instead of crystals. This explains the reason for adding vinegar when making a candy that is to be pulled.

565. Milk Sugar. $C_{12}H_{22}O_{11} \cdot H_2O$. *Lactose* has practically the same composition as cane sugar. It contains

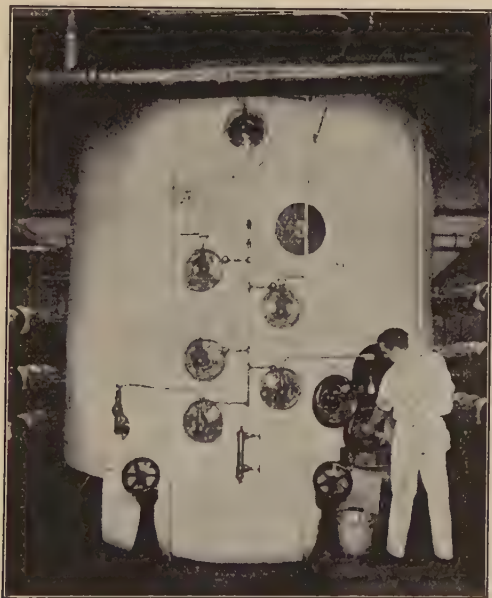


FIG. 239.—Vacuum pan for making granulated sugar.

water of crystallization. Lactose is found in milk to the extent of about 5%. Its chief use is as a food and in medicine for coating pills. Certain bacteria present in milk change the lactose by fermentation into lactic acid, which is always present in *sour milk*.

566. Maltose. $C_{12}H_{22}O_{11}$. Malt is made by germinating barley in water and then drying it. Barley contains the

enzyme diastase, which converts starch into maltose, a very sweet sugar similar to lactose. It is manufactured in large quantities for making alcoholic beverages.

567. Dextrose. $C_6H_{12}O_6$. This compound is often known as *grape sugar*, or sometimes as *glucose*. It is found in nature in grapes, various other fruits, and honey. Pure *grape sugar* is a white crystalline solid about three-fifths as sweet as cane sugar. We have seen that it is formed by the inversion of sucrose. It is prepared commercially in large quantities by heating starch with hydrochloric acid. Usually dextrose is marketed in the form of *glucose*, a thick syrupy liquid that contains both dextrose and dextrin. Large quantities of glucose are used in making candies, in molasses, jams, and jellies. It is not injurious, but it forms a highly concentrated food. The only possible objection to its use is when it is sold as a substitute for cane sugar at the same price as sugar itself.

568. Levulose. $C_6H_{12}O_6$. *Levulose* or *fructose* is found in many fruits together with glucose. It is formed in equal quantities with glucose during the inversion of cane sugar. The student will observe that it has the same formula as dextrose. Two compounds having the same percentage composition and the same molecular weight are said to be *isomeric*. Dextrose turns the plane of polarized light to the right, while levulose twists this plane to the left. This property furnishes the name for these sugars.

569. Starch. $(C_6H_{10}O_5)_n$. Starch is found in grains, seeds, tubers, and fleshy roots. Most of the starch made in the United States comes from corn, but potato starch is more common in Europe. Starch is made up of granules that vary in appearance, depending upon the source. By the aid of a compound microscope it is often possible to tell from what plant the starch was obtained. See Fig. 240. Starch is insoluble in water, but when heated the granules swell and burst, and the *altered* starch forms a colloidal

suspension. If only a little water is used a kind of transparent jelly is formed known as starch paste. Starch is used in the laundry in the form of a dilute paste. In the use of cold starch the granules suspended in water are taken up by the fabric. During the ironing the heat from the iron probably produces altered starch. With iodine, starch gives a blue-black color. This color reaction forms a test for either iodine or starch.

Enormous quantities of starch are used every year in making glucose and dextrin. It is also used in the laundry



FIG. 240.—Starch grains from various plants.

and as sizing material for finishing cloth. As a food it furnishes heat and energy. Nitric acid acts on starch to form *nitro-starch*, a compound having explosive properties. As an explosive this compound promises to become more common since starch can be prepared so cheaply.

570. Cellulose. $(C_6H_{10}O_5)_x$. Cellulose forms the basis of woody plants. Cotton and linen fibers are nearly pure cellulose. Wood is largely cellulose, and the cell-walls of various plants are made up of this important compound. Like starch, cellulose does not volatilize without decomposition, and it is insoluble in ordinary solvents. It dissolves in zinc chlorid solution and in an ammoniacal solution of copper oxid. We have already learned that nitric acid

interacts with cellulose to form the basis of smokeless powder, collodion, and celluloid. Parchment paper is made by the action of sulfuric acid on cellulose. Further treatment with sulfuric acid converts cellulose into dextrin and glucose.

571. Paper. Paper is made from cellulose which is obtained from various kinds of wood, from straw, and from linen or cotton rags. See Fig. 241. In making paper from



(Courtesy of B. D. Rising Paper Co.)

FIG. 241.—Sorting paper rags.

wood the raw material is first shredded and then treated with some reagent such as sodium hydroxid to dissolve the gummy substances and leave nearly pure cellulose. A better and stronger pulp is made by treatment with calcium bisulfite. If a white paper is desired some bleaching agent is used. When rags are used, they are cut into pieces and dusted before boiling. See Fig. 242. In the boiler of Fig. 243 about 12,000 pounds of rags are boiled at one time. To

remove the color and impurities lime and soda are used during the boiling, which is continued several hours. In the treatment of either rags or wood pulp, the mass is next converted into pulp by being run through knives placed on rollers which match a set of knives on the bedplate. See Fig. 244. From the beaters the pulp suspended in water



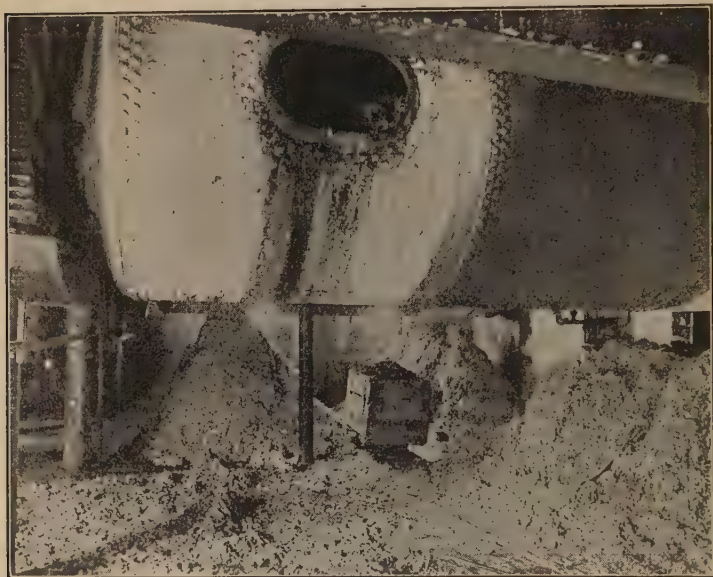
(Courtesy of B. D. Rising Paper Co.)

FIG. 242.—Rags cut and dusted ready for boiling.

is run onto screens. See Fig. 245. From the screens it passes through rollers which dry it and press it into paper. See Fig. 246. To increase the weight of paper such loading materials as clay, calcium sulfate, and barium sulfate are often added. If the weighting does not exceed 10%, it is not considered an adulterant, although some papers contain 30%. Paper that is to be used with ink is *sized* to close the pores and keep the ink from spreading. Rosin dissolved in

sodium hydroxid and then precipitated with aluminum sulfate is often used for sizing. High-grade papers are sometimes sized with gelatin.

572. Textiles. Four fibers are extensively used in the textile industry. Silk and wool are animal fibers containing nitrogen as well as carbon, hydrogen, and oxygen. Wool



(Courtesy of B. D. Rising Paper Co.)

FIG. 243.—A boiler in which 12,000 pounds of rags are boiled at one time.

also contains sulfur. Linen and cotton are nearly pure cellulose. The compound microscope furnishes the best method for identifying these fibers. The animal fibers, wool and silk, may be distinguished from the plant fibers, linen and cotton, by chemical tests. Wool and silk dissolve in a hot solution of sodium hydroxid (5%), while cotton and linen are not much affected by such treatment. On the other hand, cold concentrated hydrochloric acid hardly

affects wool and dissolves silk slowly, but it attacks the plant fibers more readily. While it is easy to distinguish cotton from linen by the use of the microscope, it is not so easy by the use of chemical reagents, especially if the linen has been laundered a few times. Cold concentrated sulfuric



(Courtesy of B. D. Rising Paper Co.)

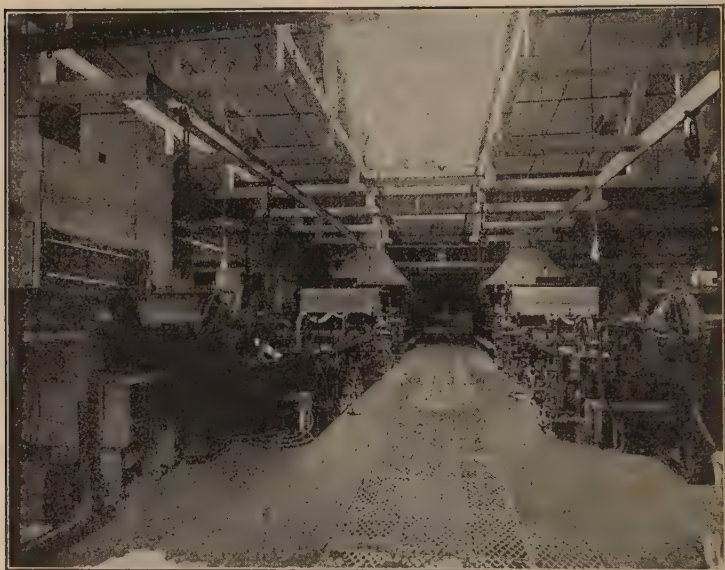
FIG. 244.—The beaters which convert the rags into pulp.

acid dissolves cotton almost completely in 2 minutes, but attacks new linen only slightly in that time (Fig. 247).

573. Mercerized Cotton. When cotton is immersed in a strong solution of sodium hydroxid it shrinks to about three-fourths of its former length. If the cloth is stretched so that shrinkage can not occur when it is immersed in the sodium hydroxid solution, the nature of the fiber is changed. It becomes stronger and assumes a luster resembling silk. Cotton so treated is said to be *mercerized*, being named from

John Mercer. Mercerized cotton takes dyes more readily than ordinary cotton.

574. Artificial Silks. Several so-called artificial silks are now being manufactured. They are not silks at all, but they are made from cellulose so treated that it has a silky sheen. *Pyroxylin silks* are made by forcing a con-



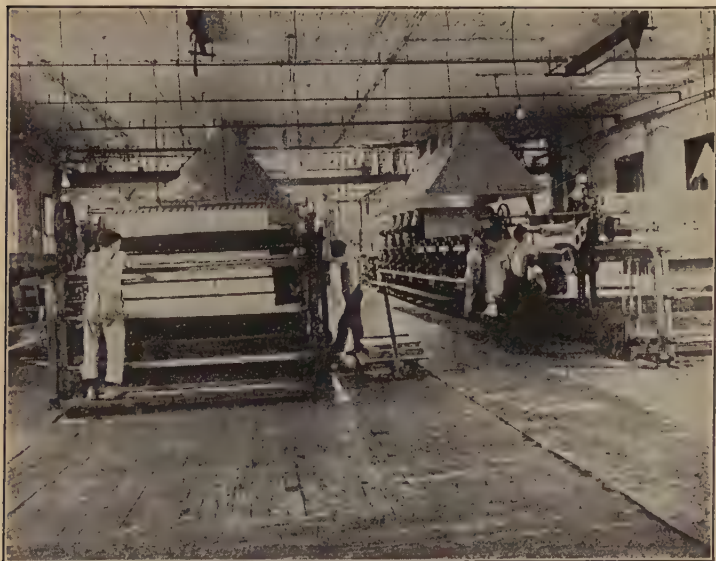
(Courtesy of B. D. Rising Paper Co.)

FIG. 245.—Wet end of a Fourdrinier paper machine.

centrated colloidal solution of nitrates of cellulose through very small capillary tubes under high pressure. The compounds solidify upon contact with the air, forming fine silky threads. To render the fibers less inflammable they are de-nitrated by the action of some alkaline sulfid. *Viscose silk* is made in a similar manner, the solution of cellulose being prepared by treating wood fibers with sodium hydroxid and then adding carbon disulfid. Artificial silks are nearly

as strong as natural silks and in some cases they have a more brilliant luster. Their tensile strength when they are wet is very much reduced. They are often known as *luster-cellulose*.

In the *cuprammonium* process short fibers of cotton that are not suitable for spinning are dissolved in an ammoniacal solution of copper. The clarified solution is then forced



(Courtesy of B. D. Rising Paper Co.)

FIG. 246.—The cutter end of a Fourdrinier paper machine.

through spinnerets, each containing 20 holes 0.005 mm. in diameter in an alloy made of gold and platinum. The colloidal solution of the cotton fibers comes out through these small holes when the spinnerets are submerged in sodium hydroxid solution. See Fig. 248. Instantly the colloid is precipitated to form a very small fiber. The twenty threads thus formed are twisted together to form a silk thread. The silk is then reeled and washed in a solution of

formic or acetic acid to neutralize the sodium hydroxid. See Fig. 249.

575. Cellulose Acetate. This compound is formed by treating cellulose with anhydrous acetic acid. It is a viscous



FIG. 247.—Fibers of cotton, wool, linen, and silk.

liquid. When it dries it forms a tough film that is water-proof and a non-conductor of electricity. It is less inflam-

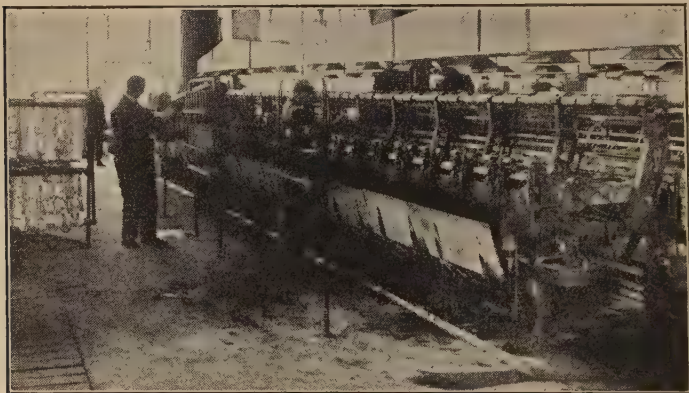


FIG. 248.—Spinning artificial silk.

mable than the nitrates of cellulose, but more brittle. It finds use as an insulator, for making artificial horsehair, in airplane construction, auto goggles, gas masks, and the

so-called safety films for motion pictures. Films made of cellulose acetate may be used without a fireproof booth in many states.

576. Wool. Wool is an animal fiber, usually obtained from the sheep, some species of goats, or from the llama, an animal found in the Andes mountains of South America. Mohair is made from the fleece of the Angora goat, and cashmere from the wool of a goat found in Tibet. Wool



FIG. 249.—Reeling and washing the silk.

contains sulfur and nitrogen in addition to carbon, hydrogen, and oxygen. In scouring wool, suint and lanolin are obtained as by-products. *Suint* is a water-soluble substance rich in potassium compounds. *Lanolin* is a wool-fat that is used in pharmacy as a vehicle for ointments.

Alkalis and oxidizing agents destroy woolen fabrics, hence a laundry soap containing much free base is not suitable for washing woolen, and chlorin is too strong an oxidizing agent to be used for bleaching woolen goods. Wool is quite hygroscopic, the amount of moisture adsorbed upon the surface of the fiber being quite marked. Wool is

sufficiently basic to combine readily with acid dyes without the use of a mordant. Wool fibers become brittle if heated much above 100° C.

577. Silk. Silk also contains nitrogen, but unlike wool, it does not contain sulfur. Silk is obtained by unwinding the cocoons spun by the silkworm. The silk-glue must be softened first in warm water before the fibers can be reeled. Like wool, silk is very hygroscopic. The determination of the amount of such water adsorbed is technically known as *conditioning*. It may amount to as much as 30% of the weight of the silk. To make silk smooth and glossy the raw product, which is quite harsh, is treated with a warm soap solution to dissolve more of the silk-glue. If the product is to be *ecru silk*, the washing is continued until the loss of weight is only 2 to 4%. If all the glue is removed the loss in weight may be as much as 25 to 30%. During the dyeing of silks tin salts are often added. Such *weighting* of silk may more than double the weight of a fabric. A silk so heavily *weighted* or *loaded* may crack very quickly.

Silks are attacked by alkalis more readily than cotton; they dissolve in hydrochloric acid readily. Strong oxidizing agents destroy the fiber. Silk is bleached with sulfur dioxide, hydrogen peroxide, or a dilute solution of potassium permanganate.

578. Dextrin. $C_6H_{10}O_5$. Dextrin is made by the action of saliva, diastase, or the pancreatic juice on starch. It may be made commercially by heating starch, or by treating it with a dilute acid. Dextrin is a sticky substance used as a substitute for gum arabic in calico printing and as an adhesive for postage stamps and envelopes. Dextrin is sometimes used in inks to make them adhere to the paper.

579. Pectin is a complex carbohydrate which forms with cellulose a compound known as pectocellulose. When certain fruits are boiled with water hydrolysis of this compound occurs, resulting in the formation of pectic acid.

Pectic acid and its salts form a jelly when cooled. Fruits will not "jell" unless they contain pectin which may be partially transformed into pectic acid. Pectin is not present in over-ripe fruits, hence they can not form a jelly. Too long boiling decomposes the pectic acid of sour fruits and prevents the formation of jellies.

580. Gums. These compounds are carbohydrates found in nature, usually secreted from the bark of certain trees. As a rule gums dissolve in water to form a mucilage, but are insoluble in alcohol. *Gum arabic*, or *acacia*, and *gum tragacanth* are two of the most common gums. They are used in preparing emulsions, in confectionery and lozenges, in calico printing, and in finishing cloth. Cherry gum is used for stiffening hats.

581. Resins. The resins contain carbon, hydrogen, and oxygen. They are hard translucent solids, generally obtained as exudations from certain trees, or they may occur as fossil mineral substances. Unlike the gums, they are insoluble in water, but they dissolve in alcohol and turpentine. Rosin, copal, lac, amber, dammar, and sandarac are some of the most important resins. They find extensive use in the varnish industry. Asphalt is sometimes classed as a fossil resin.

582. Varnishes are made by dissolving resins in a suitable solvent. A good varnish should not be discolored by the action of water. It should form a hard, translucent, lustrous coating tough enough so it will neither crack easily, nor form a resinous dust when scratched with a sharp instrument. The properties depend upon the nature of the resin and upon the solvent used, some varnishes being tough and elastic, others being hard but somewhat brittle.

Spirit varnishes are made by dissolving a resin, usually *lac*, in alcohol. Such a varnish is known as *shellac*. It gives a hard surface and dries rapidly as the alcohol evaporates. *Turpentine varnishes* usually give a tougher coating;

they are made by dissolving resins in hot turpentine. *Oil varnishes* are made by heating the melted resins with linseed oil or Chinese wood oil. They form excellent varnishes since the coat is very tough and resists the action of water very well. Copal is a resin largely used in making high-grade varnishes, while rosin is employed in the manufacture of cheap varnishes.

B. FOODS

583. Definition. Any substance taken into the body proper that furnishes *heat, energy, or nutrition* may be termed a food. Before a food can be absorbed by the body and taken into the blood it must be in a fluid or semi-fluid condition. Digestion is the process of changing insoluble substances into soluble compounds or of producing emulsions, that may be readily absorbed. For example, starch is insoluble, but in the process of digestion it is changed by the action of a ferment into glucose, a soluble compound. Albuminoid substances are changed to peptone by the ferments pepsin and trypsin. Fats and oils are emulsified or saponified.

584. Classification of Foods. Foods are made up of the three classes of nutrients: *Carbohydrates; proteins; fats and oils*. The carbohydrates include starch and the sugars. The source of sugar we have already studied, and we also learned that corn and potatoes furnish large quantities of starch. Other foods rich in starch are rice, flour, and all kinds of cereals.

Proteins, or albumins, are often called nitrogenous foods. They are very complex compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus, and iron. When derived from different sources they vary slightly. Lean meat contains protein in the form of *myosin*. The white of egg is another form of protein known as *albumen*. When milk curdles, a white nitrogenous compound known

as *casein* separates from the whey or liquid portion. The sticky substance in flour called *gluten* is another form of protein, while beans and peas contain protein in the form of *legumin*. Gelatin is a nitrogenous jelly obtained by long boiling of animal tissues. It can not wholly take the place of protein as a food.

Fats and oils are obtained from fat meat, butter, lard, and the oils from nuts and seeds.

To furnish mineral matter for the teeth and bones, such elements as calcium, phosphorus, and magnesium are needed. Iron is used in the blood, especially in the red blood cells, where it aids in carrying oxygen. It is obtained from such foods as spinach, lettuce, and other green vegetables. Mineral substances are also obtained from eggs, milk, cheese, and the outer covering of grains. Whole-wheat bread has much more mineral matter than bread made from white flour. Food as prepared for use in most American families is apt to be deficient in mineral matter.

The outer covering of grains also contains more cellulose than the inner part and consequently more indigestible matter. This is believed to act mechanically as a laxative stimulant. It has been proven in Japan and the Philippines that the disease *beri-beri* is more common when rice from which the outer covering has been removed is used as a food. In the army and navy the brown rice is now used instead of the white grain from which the hull has been polished.

Some foods contain all the nutrients in about the proportion they are needed in the body. Milk is such a food, having the following composition:

	Per cent
Water.....	88
Milk sugar.....	4-5
Fat.....	3-6
Protein.....	3-4
Mineral ash.....	0.7

Meat and eggs both contain fat and proteins, but no carbohydrates. Bread consists largely of carbohydrates with some protein. With butter it forms quite a complete food.

585. Vitamins. A food may contain all the nutrients discussed in the preceding section and yet not keep the body healthy or promote growth. Certain little-known compounds called *vitamins* must also be present. They appear to act as catalysts, but their function is unknown. It is known that children do not grow well and that certain diseases occur when the foods are lacking in vitamins. One of these vitamins is *soluble in fats*. It is found in milk and butter. Two *water-soluble* vitamins are also known. They are present in fresh vegetables and in the juices of certain fruits.

Oleomargarine may be as nutritious as butter, but it lacks vitamins, and it should not be used as a butter substitute for children. Condensed and Pasteurized milks may have their vitamins destroyed by heating. Canned foods are deficient in vitamins.

586. Value of Foods. Of several ways of determining food values, the measurement of the number of calories it can furnish is one of the most common. For example, it has been determined that one thick slice of bread will furnish 100 large calories of heat if completely oxidized. Sugar is a more concentrated food, $1\frac{1}{2}$ teaspoonfuls furnishing 100 calories.

That the above method of judging food values is not satisfactory when used alone may be seen if we inquire the purpose of the various nutrients in food. The carbohydrates are usually completely oxidized, unless eaten in excess, and thus supply *heat* and *energy* to the body. Fats and oils are not so easily oxidized, but they yield more heat and energy than the carbohydrates. Proteins are eaten to replace worn-out tissues, and for building new tissues in a growing body. Thus it is easy to see that a carbohydrate

diet might furnish all the heat and energy required daily, but growth and repair would be lacking. A mixed diet of fats and carbohydrates would still be deficient in tissue-building properties. If the diet were wholly protein, a part of the food might be oxidized to supply the needed calories, and the remainder used for nutrition. This would be objectionable for two reasons: (1) Proteins are too expensive to be used for fuel; (2) the oxidation of fats and carbohydrates gives carbon dioxid and water only, while the oxidation of proteins leaves waste products that are excreted with difficulty. Thus an excess of protein results in overworked excretory organs, especially the kidneys. From the above statements the student can see that a proper diet should contain all the nutrients, proteins for *nutrition*, fats and carbohydrates for *heat* and *energy*, and sufficient vitamins.

Several other facts should also be considered in choosing a proper diet. For example, grass has much nutritious value, but the human stomach is not fitted to digest it. Wood has heat value but it is indigestible. In addition to a knowledge of heat values and composition of foods, the following questions should be asked: (1) *What per cent of the food is digestible?* Some coarse vegetables contain a large per cent of woody tissue that is entirely indigestible. On the other hand, a considerable amount of indigestible matter is desirable so the stomach and intestines may have bulky foods for peristalsis. (2) *How much time and energy are required to digest a given food?* The student must bear in mind that part of the food already digested must furnish the energy for digesting the following meal. If too much time and energy are required in digestion, the loss of energy may be equal to the gain. (3) *Is the food liable to ferment?* If food is not digested quickly fermentation may occur, producing gas and sour stomach. Starchy foods are especially liable to ferment.

In addition to all these factors, the complexity is increased

by subjective conditions and the manner of life of the individual. To get the best results the student must study general principles and then modify them to fit his personal needs and his mode of living.

587. Cooking of Foods. Although foods are sometimes eaten raw, yet most foods are cooked before being eaten. Cooking serves at least three important purposes: (1) *It makes the food more palatable.* (2) *Cooked foods are usually more easily digested than raw foods.* (3) *Cooking destroys disease-producing bacteria that may be present in the food.* The cooking of protein foods coagulates the albumin and may in some cases make digestion rather more difficult. With starch, however, cooking breaks up the cells and makes digestion much easier; raw starch is apt to be indigestible, or digested with difficulty.

When meats are to be roasted they should be put in a hot oven to coagulate the albumin on the outside and prevent loss of the juices. The heat may then be moderated as the steam in the interior continues the cooking. Broiled meats are seared over a naked flame for the same purpose, the juices being retained by the coagulated exterior. Baking generally requires a hot oven at the beginning for the same reason. In baking bread the interior of the loaf does not rise above the temperature of the steam, which really furnishes the heat for baking the inner part of the loaf. In boiling foods, if the water in which they are cooked is to be used for broth or soups, they may be put into cold water and heated slowly. If the water is not to be used, the foods should be put in hot water to prevent loss of nutritious matter. Fried foods are not easily digested as the particles become covered with grease, and fats are not digested until the food reaches the intestine. Rather unfortunately, many persons are fond of fried foods. If the grease is hot when the food is introduced, coagulation occurs quickly and the grease does not soak into the food so readily.

588. Why Foods Spoil. The decay of foods is brought about by the action of three classes of plants: *yeasts*, *molds*, and *bacteria*. See Fig. 250. We have already learned that yeasts are capable of changing sugar into alcohol and carbon dioxid. Certain kinds of bacteria cause the decay of protein foods. In some cases disagreeable odors are given off by the gases formed, and usually the taste is very different. Pto-maines, poisonous bodies, are sometimes formed in animal foods by the action of bacteria. Although fats and oils are not so likely to spoil as the other nutrients, yet they sometimes become rancid by the action of bacteria. Molds and mildews are usually saprophytic plants, living and

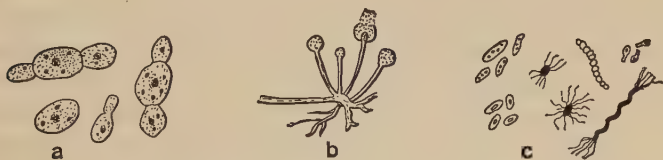


FIG. 250.—a, Yeasts; b, Mold; c, Bacteria.

feeding on dead animal and plant tissues. Thus they gradually destroy the food. In the case of some molds poisonous substances are formed and the food is unfit to eat. In other cases certain molds are harmless, and in special varieties of cheese they may impart a desirable flavor.

With the exception of the molds these plants are very small, but they grow rapidly under favorable conditions. Moisture is necessary for the growth of all of them, while sunlight is unfavorable. In fact exposure to direct sunlight for 8 or 10 hours usually destroys them. Mold will not grow on dry bread, neither does sugar ferment unless it is in solution. The temperatures also affect the growth of these organisms. Most of them do not grow at 32° F. and few of them survive the temperature of boiling water. A temperature of 70° to 90° F. is very favorable to their rapid

growth. Although these plants may live for a short time without food, yet they can not multiply without it. They generally reproduce by simple division; thus one bacterium may divide to form two, these two may subdivide to form four, and so on. Under favorable conditions, temperature, moisture, and food supply, this fission may occur every 30 minutes. These organisms also develop spores which are so light that they are readily carried by the wind; in this manner they find their way into exposed foods, where they soon begin to grow. These spores often develop a thick wall and are capable of resisting drought and extremes of temperature.

589. Preservation of Foods. Many ways of preserving food are in common use, all of them designed to destroy the organisms that promote decay or to prevent their coming into contact with the food.

One of the earliest methods of preserving food, and one that should be used more extensively in this country at the present time consists in *dehydrating* the food, or in removing the water that most foods contain so abundantly. We should remember that the organisms that produce decay can not thrive unless moisture is present. Evaporated and condensed milk are more easily preserved than normal milk, on account of the removal of part of the water. In condensed milk sugar is also added as a preservative. Powdered milk is also coming into use, especially for cooking, baking, and the preparation of ready-mixed flours. It is made by partially evaporating the milk in vacuum pans and then spraying the remaining liquid through very small openings into a room heated by hot air. The rest of the water evaporates, leaving the milk as a white powder. Other foods preserved by *drying* are fruits, such as prunes, raisins, figs, apricots, etc. Corn and peas may be preserved in the same manner.

Canning food in tin cans or in glass jars is a common

method of preserving foods. The food is heated to the boiling point, or above in some cases, to kill the organisms that produce decay, and put into the container which is then sealed air-tight. Food properly canned will keep indefinitely. If the spores have not been killed by the heating the food will eventually be spoiled. The spores of yeast are more easily destroyed by heat than bacteria and their spores. The fermentation of fruits is usually caused by yeasts, since bacteria do not grow readily in an acidic solution. Vegetables are more difficult to preserve since the spores of the bacteria that cause them to spoil are not killed unless the boiling is continued at least 1 hour; or unless the food is boiled twice with an interval between sufficient to permit the spores to develop.

A concentrated sugar solution does not ferment, but a dilute solution is quickly acted upon by the wild yeasts that float in the air. Thus foods are *preserved* by adding to them large quantities of sugar.

Vinegar is another common substance in which the germs that produce decay do not grow readily. This liquid is used in preserving foods, the process being known as *pickling*.

Meats are preserved by the addition of *salt*, or by exposing them to the action of *smoke* for some time. The process is known as *curing*. The active preservative in the smoke is probably a *cresol*. When certain woods are used to produce the smoke, an agreeable flavor is imparted to the meat. Hickory bark is extensively used. Meats may be dried to preserve them.

Refrigeration is employed when foods are to be kept a comparatively short time. At the freezing temperature of water, or in a refrigerator near this temperature, bacteria multiply slowly and food may be kept for several days. Certain molds, however, may develop quite rapidly at this temperature. Enormous quantities of food are kept in *cold storage*. In such a plant cold brine circulates through

pipes in the storage rooms and keeps them at a temperature near the freezing point.

Many *chemical preservatives* are very efficient, but their use does not meet with popular favor. A small quantity of *formaldehyd* will keep milk sweet for days, but its use as a preservative is illegal. *Salicylic acid* and its sodium salt are excellent preservatives, but objection is made to their use. *Sodium benzoate* is a chemical preservative whose use in small quantities is permitted by the U. S. government. *Sulfur dioxid* and certain *sulfites* are used to bleach molasses, dried fruits, and to some extent as a preservative of certain foods. *Potassium nitrate* is used as a preservative in corned beef and smoked meats. *Boric acid* and *borax* occasionally find use as preservatives.

There is no doubt but that some of these preservatives have toxic properties. The chief objection to some of them lies in the fact that they destroy organisms that cause fermentation. Since pepsin in the stomach, and amylopsin, trypsin, and steapsin in the intestines are all ferments that produce digestion, it is claimed that chemical preservatives in food also interfere with digestion by arresting their action. On the other hand, ptomaines developed by bacteria in certain foods are deadly poisons and the products of decay are dangerous. Which is the lesser of the two evils, a possibility of disordered digestion from the action of the preservative, or illness from the poisonous products of decay, is a question that deserves more investigation than it has yet received, especially when we consider that the dose of sodium salicylate as given in the U. S. Pharmacopœia is 15 grains. The argument that canneries could put up partially spoiled foods if the use of chemical preservatives were generally permitted is further urged against them.

590. Food Adulterants. *Any substance mixed with a food to increase its weight or bulk is classed as an adulterant.* Preservatives are sometimes classed as adulterants. The sub-

stance used depends upon the nature of the food and is always some cheaper substance. Since the adulterant is added with intent to deceive, it generally very closely resembles the pure product. While oleomargarine may be used to adulterate butter, yet it is needless to test oleomargarine to see whether it has been adulterated with butter. Meats and eggs are seldom adulterated, although inferior cuts of meat may be substituted for more expensive ones. Flour is sometimes adulterated with gypsum and low-grade flours are substituted for high-grade wheat flour. Olive oil is frequently adulterated with cottonseed oil. Water is the most common adulterant of milk. Extracts are frequently adulterated with cheaper substitutes. The adulteration of foods in the United States is not nearly so common as it was before the Pure Food Law of 1906 was enacted.

591. Coal-tar Compounds. Several coal-tar compounds are used in foods and many important drugs are obtained from this source. Seven of the coal-tar colors are considered harmless and the United States permits their use for coloring candies, jellies, butter, and other foods. *Saccharin* is a coal-tar product more than 500 times as sweet as cane sugar. It was at one time used quite extensively to sweeten canned goods, but at the present time such use is illegal. *Coumarin* and artificial *vanillin* are coal-tar products used as flavors. We have already learned that benzoic acid and salicylic acid are preservatives. Salicylic acid and its salts are also used as medicine. *Aspirin* and *acetanilid* are used in headache powders and anti-pain pills, but the use of acetanilid is attended with considerable danger.

592. Disinfectants and Antiseptics. A chemical substance that destroys disease-producing bacteria is known as a *disinfectant*. Formaldehyd is one of the best disinfectants, since its vapor so readily penetrates to all parts of a room. Other substances often used are sulfur dioxid, chlorid of lime, carbolic acid, cresols, and bichlorid of mercury.

An *antiseptic* is a substance used to prevent or check the growth of putrefactive, or pus-forming bacteria. It differs from a disinfectant in the fact that it may be applied to living tissues without much injury to them. Iodin, iodoform, hydrogen peroxid, boric acid, and very dilute solutions of carbolic acid and bichlorid of mercury are commonly used antiseptics. Of course these substances are also preservatives. Together with other chemicals they are sometimes classed as germicides. Dakin's solution began to be used extensively during the War.

593. Alkaloids. The alkaloids are nitrogenous compounds obtained from plants. Since they often give to a plant its chief characteristics they are sometimes known as the *active principles* of plants. Many of them are used as medicines, although with few exceptions they are very poisonous. They are analogous to ammonia from the fact that they unite with acids by direct addition. *Quinine* is an alkaloid extracted from cinchona trees. Its hydrobromid and sulfate are extensively used in medicine, especially in the treatment of malaria. *Cocaine*, obtained from coca leaves, is an important local anesthetic. *Caffeine* is an active stimulant found in coffee and tea. *Codeine* is an alkaloid extracted from opium, as is *morphine*. Both alkaloids are used to allay pain. Paregoric and laudanum are prepared from opium. *Nicotine* is a very poisonous compound found in tobacco. *Strychnine* is an active poison that occurs in *nux vomica*. *Atropine* is an alkaloid found in belladonna. It is used by optometrists to dilate the pupil of the eye. *ptomaines* are alkaloids formed in dead animal tissues.

While such alkaloids as morphine and cocaine are very valuable drugs, they should never be used unless prescribed by a physician as they are habit-forming drugs.

594. Poisons and Antidotes. In addition to the alkaloids mentioned in the preceding section, many metallic com-

pounds are poisonous. In fact soluble compounds of arsenic, antimony, barium, zinc, tin, lead, copper, mercury, and silver are all more or less active poisons. Several phosphorus compounds are poisonous, and certain groups of elements like the cyanid group are extremely poisonous.

An *antidote* is some substance used to counteract a poison. It may destroy the effect of the poison by neutralization, or it may unite with it to form an insoluble compound which is not absorbed by the digestive tract. Three general rules may be given that should be followed in case of poisoning: (1) Give an emetic to produce vomiting. Ipecac is usually most successful, as it contains the alkaloid *emetine*, a very nauseating compound. (2) Give an antidote, if the nature of the poison is known. (3) Give a purgative, such as castor oil or Epsom salts, to remove the poison from the intestines. Very often the poison is unknown and no special antidote can be given. Fortunately albumin forms an insoluble compound with the salts of most metals, and the whites of eggs and milk may be used freely, as the treatment can do no harm. If a *narcotic* poison, such as *opium*, *morphine*, or *nicotine*, has been taken, a stimulant like strong coffee should be given in quantity. *Alcohol is not a stimulant, but a narcotic*. In any case, do not let the person sleep, but keep him moving. The inhalation of ammonia is beneficial. For a *stimulant* poison like *strychnine*, a sedative such as sodium bromid may be used, or a narcotic like chloral.

For *acid* poisoning, use sodium bicarbonate, soapsuds, chalk, or magnesia.

For *alkali* poisoning, use vinegar, lemon juice, or orange juice.

Arsenic. Milk; raw eggs; freshly precipitated ferric hydroxid. Such rat poisons as "rough on rats" contain arsenic, as does also Paris green.

Bichlorid of Mercury. For this and other mercury compounds use milk freely; white of eggs; zinc sulfate.

Carbolic Acid. Alcohol; raw eggs; Epsom salts.

Hydrocyanic Acid. Ferrous sulfate followed by small quantities of potassium carbonate; artificial respiration; inhaling ammonia.

Iodin. Starchy foods in abundance; "hypo."

Lead Salts. Epsom salts; milk; albumin.

Phosphorus. Copper sulfate; Epsom salts. Avoid oils.

Potassium Cyanid. Ferrous sulfate. Artificial respiration.

Silver Nitrate. Sodium chlorid, or common table salt.

Tartar Emetic. Milk; eggs.

SUMMARY

The *carbohydrates* contain *carbon*, *hydrogen*, and *oxygen*; they include sugars, starch, cellulose, dextrin, and certain gums.

Cane sugar, beet sugar, and maple sugar all contain sucrose, $C_{12}H_{22}O_{11}$. When sucrose is heated to $210^{\circ} C$. it is converted into *caramel*. When treated with acids *inversion* occurs, resulting in the formation of dextrose and levulose. These sugars are *isomeric*; they have the same formula, the same molecular weight, but differ in properties.

Lactose, or milk sugar, contains water of crystallization. All the sugars are used as foods.

Starch is a white amorphous substance made by plants that have green coloring matter. It is a good food, it finds use in the laundry, and in finishing cloth. With iodine it produces a blue-black color.

Cellulose forms the framework for woody plants. It is used in the textile industry, for making explosives, paper, celluloid, and artificial silk.

Dextrin is made from starch. It finds use as a mucilage and in calico printing.

Gums and *resins* also contain carbon, hydrogen, and oxygen. The gums are *water soluble* or at least partially so, but *insoluble* in alcohol. The reverse is true of the resins. Resins are used in the varnish industry. Spirit varnishes consist of shellac dissolved in alcohol. Turpentine varnishes consist of turpentine in which a resin has been dissolved. Oil varnishes are made from linseed oil or China wood oil and such resins as copal, amber, dammar, and sandarac. Rosin is used in cheap varnishes.

A substance taken into the body that supplies to it heat, energy, or nourishment is termed a *food*. Digestion is the process of changing insoluble foods into soluble compounds.

Carbohydrates, proteins, and fats or oils form the *three classes* of nutrients needed by the body. Mineral matter is also essential to the body.

The value of a food may be determined by the number of calories it yields upon oxidation, by the relative proportion of the three nutrients it contains, by the ease with which it is digested, by the amount of indigestible matter, and by its liability to ferment. It must contain vitamins.

Foods are cooked to make them more palatable, to promote digestion, and to destroy any bacteria that may be present. Baking, roasting, and boiling are all excellent methods of cooking foods.

Bacteria, yeasts, and molds are three types of microorganisms that cause food to ferment or decay. They thrive at moderate temperature, on a moist surface, protected from sunlight, provided they have plenty of food material.

Foods are preserved by destroying these organisms and preventing their coming into contact with the food thus sterilized. The various methods include *drying, canning, preserving with sugar, pickling, salting and smoking, cold storage*, and the use of *chemical preservatives*.

A substance mixed with a food to increase its weight or its bulk is termed an *adulterant*. Chemical preservatives are often classed as adulterants. The adulterant used is always some cheaper product.

Both *disinfectants* and *antiseptics* destroy bacteria that produce disease. *Antiseptics* are of such a nature they may be applied to living tissues.

An *alkaloid* is a nitrogenous compound obtained from plants. Some alkaloids find use in medicine.

An *antidote* is a substance used to counteract a poison. In case of poisoning give an *emetic*, then an *antidote* if possible, and follow with a *cathartic* to remove the poison from the intestines.

QUESTIONS

1. What is a carbohydrate? Name at least three, giving their formulas.

2. What is meant by the inversion of sugar? How is it produced?

3. Why is vinegar added to a candy that is to be pulled? Would it do as well to start with glucose?
4. Discuss the commercial importance of cellulose.
5. How does "smokeless powder" differ from pyroxylin silk?
6. What is meant by loading paper? By sizing paper?
7. How would you distinguish cotton from linen? Cotton from wool? Wool from silk? Silk from luster-cellulose?
8. What are the characteristics of a good varnish? How would you test a varnish?
9. Why should a proper menu contain all the various food nutrients?
10. What purpose does each of the three nutrients serve in the body?
11. Why do we relish buckwheat cakes with butter and syrup more in January than in July?
12. What is the objection to eating raw potatoes? Raw meats?
13. Outline several methods of preserving foods. Upon what principle is each method based?
14. Why are chemical food preservatives also good antiseptics?
15. Give examples of several food adulterants.
16. What principles are involved in the use of antidotes to poisons?

APPENDIX

USEFUL TABLES

TABLE 1.—METRIC-ENGLISH EQUIVALENTS

1 inch equals 2.54 centimeters.
 1 ounce equals 28.35 grams.
 1 pound equals 453.6 grams.
 1 meter equals 39.37 inches.
 1 liter equals 1.056 liquid quarts.
 1 kilogram equals 2.2046 pounds.

TABLE 2.—THERMOMETER CONVERSION TABLE

To convert Centigrade readings into the corresponding Fahrenheit readings, multiply the Centigrade reading by 1.8, and add 32 degrees.

To convert Fahrenheit readings into the corresponding Centigrade readings, subtract 32 degrees from the observed Fahrenheit reading and divide by 1.8.

TABLE 3.—VAPOR TENSION OF WATER IN MILLIMETERS OF MERCURY

°C.	mm.	°C.	mm.	°C.	mm.
0	4.6	21	18.5	30	31.5
5	6.5	22	19.6	35	41.6
10	9.1	23	20.9	40	54.9
15	12.7	24	22.2	50	92.0
16	13.5	25	23.5	60	148.9
17	14.4	26	25.0	70	233.3
18	15.3	27	26.5	80	354.9
19	16.3	28	28.1	90	525.5
20	17.4	29	29.8	100	760.0

TABLE 4.—TABLE OF SOLUBILITIES

S, soluble in water. A, soluble in acids, insoluble in water. P, partially soluble in water, soluble in dilute acids. I, insoluble in dilute acids and in water. a, slightly soluble in acids, insoluble in water.

	Acetates	Bromids	Carbonates	Chlorates	Chlorids	Chromates	Hydroxids	Iodids	Nitrates	Oxids	Phosphates	Silicates	Sulfates	Sulfids
Aluminum..	S	S	...	S	S	...	A	S	S	A	A	a	S	A
Ammonium..	S	S	S	S	S	S	S	S	S	...	S	...	S	S
Barium....	S	S	A	S	S	A	S	S	S	S	A	A	I	..
Calcium....	S	S	A	S	S	P	P	S	S	P	A	A	A	S
Copper.....	S	S	A	S	S	S	A	S	S	A	A	A	S	A
Iron''.....	S	S	A	S	S	...	A	S	S	A	A	A	S	A
Iron'''.....	S	S	...	S	S	S	A	S	S	A	A	A	S	A
Lead.....	S	a	A	S	a	a	A	P	S	A	A	A	a	A
Magnesium..	S	S	A	S	S	S	A	S	S	A	A	A	S	A
Manganese..	S	S	A	S	S	S	A	S	S	A	A	A	S	A
Mercury'...	P	a	A	S	a	A	...	A	S	A	A	...	P	A
Mercury''..	S	S	A	S	S	P	...	A	S	A	A	...	S	A
Potassium..	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Silver.....	P	I	A	S	I	A	...	I	S	A	A	...	P	A
Sodium....	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Tin''.....	S	S	...	S	S	A	A	S	...	A	A	...	S	A
Tin'''.....	S	S	...	...	S	...	A	S	...	A	A	...	S	A
Strontium..	S	S	A	S	S	P	A	S	S	P	A	A	A	S
Zinc.....	S	S	A	S	S	S	A	S	S	A	A	A	S	A

TABLE 5.—SOLUBILITY OF GASES IN WATER

Volume of gas (reduced to S. T. P.) that can be dissolved in 1 volume of water.

Gas	0° C.	10° C.	20° C.
Hydrogen.....	0.0215	0.0195	0.0182
Nitrogen.....	0.0238	0.0196	0.0164
Air.....	0.0288	0.0226	0.0187
Oxygen.....	0.0490	0.0380	0.0310
Carbon dioxid.....	1.713	1.194	0.878
Chlorin.....		3.095	2.260
Hydrogen sulfid.....	4.686	3.520	2.672
Sulfur dioxid.....	79.79	56.65	39.37
Hydrogen chlorid.....	506.7	473.9	442.0
Ammonia.....	1298.9	910.4	710.6

TABLE 6.—SOLUBILITY OF SALTS

The numbers give the number of grams of anhydrous salt that can be dissolved in 100 grams of water at the given temperatures.

Salt	0° C.	20° C.	60° C.	100° C.
Calcium hydroxid.....	0.18			0.08
Calcium sulfate (gypsum).....	0.24			0.222
Mercuric chlorid.....	4.4	6.5	14.0	54.0
Potassium sulfate.....	7.6	11.3	17.8	24.3
Potassium chlorate.....	3.5	7.5	26.0	56.0
Potassium nitrate.....	13.4	26.0	110.0	246.0
Copper sulfate.....	14.7	21.7	39.0	73.5
Sodium chlorid.....	35.5	36.3	37.9	39.8
Potassium chlorid.....	28.5	34.0	45.2	56.3
Potassium bromid.....	54.5	65.3	86.0	105.0
Sodium nitrate.....	73.0	88.0	125.0	176.0

TABLE 7.—PHYSICAL CONSTANTS OF IMPORTANT ELEMENTS

Name	Valence	Specific weight		Melting point	Boiling point
		Water	Air		
				degrees C.	degrees C.
Aluminum.....	3	2.7		657	2200
Antimony.....	3, 5	6.62		630	1600
Arsenic.....	3, 5	5.73		sublimes	
Barium.....	2	3.8		850	950
Bismuth.....	3, 5	9.78		270	1435
Boron.....	3	2.45		infusible	3500
Bromin.....	1, 3, 5	3.1		—7.3	59
Calcium.....	2	1.54		810	
Carbon.....	4	1.7-3.5		infusible	3600
Chlorin.....	1, 3, 5, 7		2.49	—102	—33.6
Chromium.....	2, 3, 6	6.9		1520	2200
Cobalt.....	2, 3	8.72		1480	
Copper.....	1, 2	8.9		1083	2310
Fluorin.....	1		1.31	—223	—187
Gold.....	1, 3	19.3		1063	2530
Hydrogen.....	1		.069	—259	—252
Iodin.....	1, 5, 7	4.9		114	184
Iron.....	2, 3	7.86		1530	2450
Lead.....	1, 2, 3, 4	11.34		327	1525
Magnesium.....	2	1.74		650	1120
Manganese.....	2, 3, 4, 6, 7	7.4		1260	1900
Mercury.....	1, 2	13.56		—38.8	357
Nickel.....	2, 3	8.7		1450	
Nitrogen.....	1, 2, 3, 4, 5		0.96	—213	—195
Oxygen.....	2		1.10	—218	—182
Phosphorus.....	3, 5	1.8-2.3		44.1	290
Platinum.....	4	21.4		1755	
Potassium.....	1	0.87		62.5	757
Radium.....	2				
Silicon.....	4	2.4		1420	3500
Silver.....	1	10.5		961	1952
Sodium.....	1	0.97		97.6	877
Strontium.....	2	2.5		900	
Sulfur.....	2, 4, 6	2.0		114.5	444.6
Tin.....	2, 4	7.0-7.3		232	2200
Tungsten.....	6	18.7		3000	
Zinc.....	2	7.1		419	918

TABLE 8.—HEAT OF FORMATION OF COMPOUNDS

The numbers show the number of large calories of heat liberated during the formation of one mole of the compound. The minus sign indicates that heat is absorbed during the formation of the compound.

Name of compound	Symbol	Heat of formation
Hydrogen oxid (water).....	H ₂ O	68.4
Hydrogen peroxid.....	H ₂ O ₂	45.2
Hydrogen chlorid.....	HCl	22.0
Hydrogen bromid.....	HBr	8.4
Hydrogen iodid.....	HI	—6.1
Hydrogen fluorid.....	HF	37.6
Hydrogen nitrid (ammonia).....	NH ₃	12.0
Hydrogen sulfid.....	H ₂ S	4.8
Nitric acid.....	HNO ₃	41.6
Sulfuric acid.....	H ₂ SO ₄	192.9
Sodium hydroxid.....	NaOH	102.0
Potassium hydroxid.....	KOH	104.6
Sulfur dioxid.....	SO ₂	71.0
Carbon dioxid.....	CO ₂	97.0
Carbon monoxid.....	CO	29
Phosphorus pentoxid.....	P ₂ O ₅	369.7
Magnesium oxid.....	MgO	146.0
Calcium oxid.....	CaO	131.5
Zinc oxid.....	ZnO	86.0
Cupric oxid.....	CuO	37.2
Mercuric oxid.....	HgO	21.5
Ferric oxid.....	Fe ₂ O ₃	195.6
Magnetic iron oxid.....	Fe ₃ O ₄	268.0
Silver oxid.....	Ag ₂ O	7.0
Aluminum oxid.....	Al ₂ O ₃	392.6
Sodium sulfate.....	Na ₂ SO ₄	328.1
Potassium sulfate.....	K ₂ SO ₄	344.3
Sodium chlorid.....	NaCl	97.9
Potassium chlorid.....	KCl	105.7

TABLE 9.—COMPOSITION OF ALLOYS

	Name	Composition
Aluminum..	Magnalium Aluminum copper	Aluminum, 90–98 per cent.; magnesium, 2–10 per cent. Aluminum, 95–97 per cent.; copper, 3–5 per cent.
Bismuth...	Wood's metal Rose's metal	Bismuth, 50 per cent.; lead, 25 per cent.; tin, 12.5 per cent.; cadmium, 12.5 per cent. Bismuth, 82 per cent.; lead, 9 per cent.; tin, 9 per cent. Bismuth, 50 per cent.; lead, 25 per cent.; tin, 25 per cent.
Copper....	Brass Bronze Gun metal Bell metal Copper coins Nickel coins Aluminum bronze German silver	Copper, 60–80 per cent.; zinc, 20–40 per cent.; lead, 0.1 per cent. Copper, 92 per cent.; tin, 8 per cent. Copper, 90 per cent.; tin, 10 per cent. Copper, 75 per cent.; tin, 25 per cent. Copper, 95 per cent.; tin, 4 per cent.; zinc, 1 per cent. Copper, 75 per cent.; nickel, 25 per cent. Copper, 90–98 per cent.; aluminum, 2–10 per cent. Copper, 50 per cent.; nickel, 25 per cent.; zinc, 25 per cent.
Gold.....	U. S. coins 18-karat gold 14-karat gold 10-karat gold	Gold, 90 per cent.; copper, 10 per cent. Gold, 75 per cent.; copper, 25 per cent. Gold, 58.3 per cent.; copper, 41.7 per cent. Gold, 41.6 per cent.; copper, 58.4 per cent.
Iron.....	Steel Nickel steel Chromium steel Manganese steel Tungsten steel Molybdenum steel	Iron, 99.8–98 per cent.; carbon, 0.2–2 per cent. Iron, 94 per cent.; nickel, 5 per cent.; carbon, 1 per cent. Iron, 95–97 per cent.; chromium, 2–4 per cent.; carbon, 1 per cent. Iron, 92 per cent.; manganese, 7 per cent.; carbon, 1 per cent. Iron, 91–92 per cent.; tungsten, 7–8 per cent.; carbon, 1 per cent. Iron, 94.5–96 per cent.; molybdenum, 3–4 per cent.; carbon, 1–1.5 per cent.
Lead.....	Solder Pewter Type metal	Lead, 33–66 per cent.; tin, 33–66 per cent. Lead, 18–75 per cent.; tin, 25–82 per cent. Lead, 80 per cent.; tin, 5 per cent.; antimony, 15 per cent.
Mercury...	Tin amalgam Silver amalgam Copper amalgam	Tin and mercury, variable proportions. Silver and mercury, variable proportions. Copper and mercury, variable proportions.
Silver.....	U. S. coins Sterling	Silver, 90 per cent.; copper, 10 per cent. Silver, 92.5 per cent.; copper, 7.5 per cent.
Tin.....	Britannia Babbitt	Tin, 85 per cent.; antimony, 10 per cent.; copper, 2 per cent.; zinc, 3 per cent. Tin, 45.5 per cent.; lead, 40 per cent.; antimony, 13 per cent.; copper, 1.5 per cent.

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LIST OF ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS. (O = 16.)

The most important elements are printed in heavy type.

Name of element	Symbol	Atomic weight	Name of element	Symbol	Atomic weight
Aluminum	Al	27.1	Molybdenum...	Mo	96.0
Antimony	Sb	120.2	Neodymium....	Nd	144.3
Argon	A	39.9	Neon.....	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton.....	Nt	222.0
Bismuth	Bi	209.0	Nitrogen	N	14.008
Boron	B	10.9	Osmium.....	Os	190.9
Bromin	Br	79.92	Oxygen	O	16.00
Cadmium.....	Cd	112.4	Palladium.....	Pd	106.5
Cæsium.....	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.1
Cerium.....	Ce	140.25	Praseodymium..	Pr	140.9
Chlorin	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium.....	Rh	102.9
Cobalt	Co	58.97	Rubidium.....	Rb	85.45
Columbium....	Cb	93.1	Ruthenium.....	Ru	101.7
Copper	Cu	63.57	Samarium.....	Sa	150.4
Dysprosium....	Dy	162.5	Scandium.....	Ss	45.1
Erbium.....	Er	167.7	Selenium.....	Se	79.2
Europium.....	Eu	152.0	Silicon	Si	28.1
Fluorin	F	19.0	Silver	Ag	107.88
Gadolinium....	Gd	157.3	Sodium	Na	23.00
Gallium.....	Ga	70.1	Strontium	Sr	87.63
Germanium....	Ge	72.1	Sulfur	S	32.06
Glucinum.....	Gl	9.1	Tantalum.....	Ta	181.5
Gold	Au	197.3	Tellurium.....	Te	127.5
Helium.....	He	4.00	Terbium.....	Tb	159.2
Holmium.....	Ho	163.5	Thallium.....	Tl	204.0
Hydrogen	H	1.008	Thorium.....	Th	232.15
Indium.....	In	114.8	Thulium.....	Tm	169.4
Iodin	I	126.92	Tin	Sn	118.7
Iridium.....	Ir	193.1	Titanium.....	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton.....	Kr	82.92	Uranium.....	U	238.2
Lanthanum....	La	139.0	Vanadium.....	V	51.0
Lead	Pb	207.2	Xenon.....	Xe	130.2
Lithium	Li	6.94	Ytterbium.....	Yb	173.5
Lutecium.....	Lu	175.0	Yttrium.....	Yt	89.33
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium.....	Zr	90.6
Mercury	Hg	200.6			



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